



Fouling Control in Ceramic Nanofiltration: Forward flush and precoating method

MSc Thesis – Fajar Muhammad Rahman

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Environmental Engineering

Fouling Control in Ceramic Nanofiltration

Forward Flush and Pre-coating Method

By

Fajar Muhammad Rahman

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Thesis committee:

Prof. dr. ir. L.C. Rietveld
Dr. Sebastian G. J. Heijman
Ir. Franca Kramer
Dr. Claire Chassagne,

TU Delft
TU Delft
TU Delft
TU Delft

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Abstract

The new concept of sewer mining which utilizes the ceramic nanofiltration (C-NF) membranes offers a compact solution for water and other resources recovery. However, since it has very limited pre-treatment process, membrane fouling is a common problem due to the direct contact between the membrane and sewage water. Sewage water contains a lot of extracellular polymeric substances (EPS) that can block the membrane pores. One of the most persistent EPS is sodium alginate which responsible for the gel layer formation on the membrane surface.

Removal of the alginate gel layer can be done by implementing chemical cleaning. However, too frequent chemical cleaning can damage the membrane and environmentally dangerous. Therefore, to make this new concept of sewer mining more feasible, the correct cleaning method to remove the fouling layer need to be found. From this point, the research objective for this research is formulated as “Investigation of fouling control methods that can prolong the time before chemical cleaning needs to be performed to achieve higher water production.”

Several methods such as forward flush, iron coating and calcium carbonate coating was investigated. Alginate filtration was done under constant pressure experiment and the effectivity of each cleaning method was calculated by measuring the change in water permeability after the cleaning. The results show that the iron and calcium carbonate coating followed by 5 min forward flush are able to achieve a permeability recovery of 40 to 90 %. Iron coating required 400 mg/l of iron hydroxide to be dosed and a minimum of 5 min reaction times with hydrogen peroxide to have a high permeability recovery. On the other hand, only 1 minute is required by 200 mg/l calcium carbonate dosing concentration with citric acid as a cleaning solution to achieve a similar improvement as the iron hydroxide coating. Both of the processes produce higher water productivity in 2 h of experiment than the chemical cleaning with 0.1 % sodium hypochlorite.

In the end, a theoretical projection on the real sewage water filtration was made to study the economic and environmental impact of the coating process. The results show the cost of production per m³ of clean water is 0.22 euro for iron hydroxide and only 0.12 euro for calcium carbonate. Furthermore, environmental impact assessment using Chain Management by Life Cycle Analysis (CMLCA) software which produced by Leiden University with Eco-indicator 99 (EI-99) categorization shows that calcium carbonate has less environmental burden than iron hydroxide coating.

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1 Introduction

1.1. Wastewater reclamation

Inadequate water supply and low water quality are common problems faced by many countries. Europe is no exception; it was predicted that in the coming 50 years the southern parts of the European continent will suffer from severe water stress. Those regions will have high water withdrawal to availability ratio even if they lower water consumption per capita [1]. As a result, the implementation of wastewater reuse is increasingly essential to secure water supply stability [2].

Development in water reuse and reclamation from municipal sewage water introduce a new concept of recovery which is called sewer mining [3]. Sewer mining is a decentralized water reclamation concept where municipal sewage water is considered as a valuable resource instead of waste. In this concept water and other critical resources will be treated and reclaimed. As a final product, treated water can be used directly on the spot or utilized for non-potable usage [4].

Developments in water treatment technology, specifically in reverse osmosis (RO), offer excellent opportunities to improve the quality of water reclaimed during sewer mining. RO can produce water with a small amount of impurities due to its small molecular weight cut-off. Low mineral water produced by RO filtration can then be used for industrial purposes. However, the small pores of RO membrane have as a drawback that suspended or dissolved solids (foulant) can be attached to the membrane surface, fouling the membrane [5]. Therefore, extensive pre-treatment is required to eliminate foulant in the sewage water.

In general, pre-treatment of RO aims at a high removal of the large foulant, so the RO membrane will only deal with minerals and other smaller molecules as impurities. In the water reclamation, particulate removal is mainly done by primary and secondary settling tank followed by chlorine addition and micro or ultrafiltration [6].

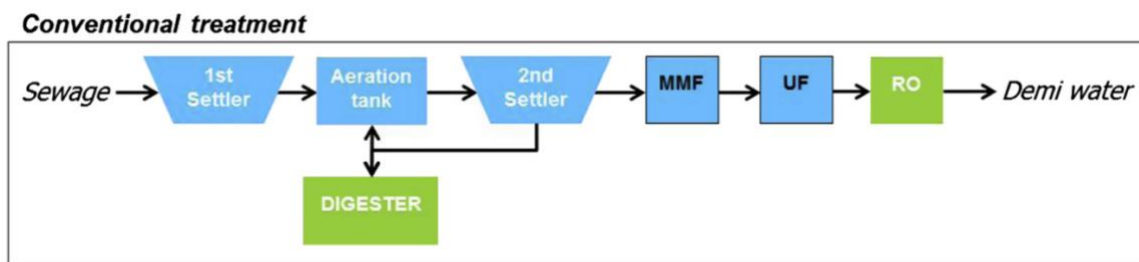


Figure 1.1: Conventional water reclamation scheme [4]

However, the concept mentioned above has some disadvantages. A large area of land is required to build primary and secondary separation. It triggers a new initiative to replace the first four units (1st settler, aeration tank, 2nd settler and MMF) with only two processes, which are a fine sieve and ceramic tight ultrafiltration (C-UF) or nanofiltration (C-NF) membrane. This new concept not only

provides less processes to produce a high quality water but each process has also a smaller footprint compared to each tank that is used in the old set-up.

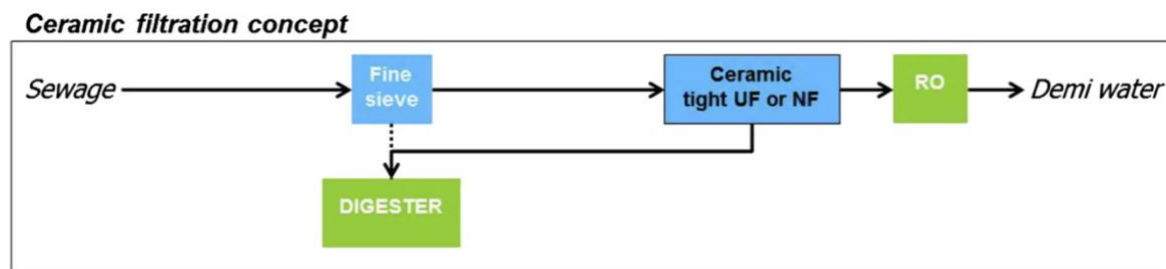


Figure 1.2: Ceramic filtration concept [4]

1.2. Problem statement

Since in the modern water reclamation concept, the water will only be treated by fine sieves before it undergoes a ultra- or nanofiltration process, there will be more colloidal particles attached to these membranes. As a consequence, severe fouling is more likely to happen, and more intensive cleaning will be required. In most practices, during a certain filtration period cleaning with a strong chemical to remove the colloid layer will be necessary. Thus membranes should be able to cope with such a chemical. The common polymeric membranes are not suitable for this cleaning process. Thus, ceramic membranes which have a higher chemical resistance will be a better choice for this new concept.

Despite having better chemical resistance compared to the polymeric membrane, too frequent chemical cleaning can still damage the ceramic membrane structure [7]. Therefore, it is necessary to prolong the filtration period before chemical cleaning need to be done. This will also result in a higher water production. Longer filtration period before chemical cleaning can be achieved by taking fouling control measures, which include physical cleaning, or secondary layer formation on the membrane surface. Since there is only limited information about fouling control of ceramic nanofiltration membrane, investigation in this area is essential.

1.3. Research objective

Based on the discussion above it can be concluded the concept of water reclamation by applying ceramic nanofiltration (NF) membrane as a step is a promising future technology. However, proper cleaning methods and operation need to be identified to achieve stable filtration operation, which leads to the formulation of the objective as:

“Investigation of fouling control methods that can prolong the filtration time, before chemical cleaning needs to be performed, to achieve a higher water production.”

1.4. Research question and approach

Based on the aforementioned objective, the research question was constructed as follow:

1. *What is/are (a) potential physical cleaning method(s) that can be applied on a ceramic NF membrane?*
2. *How effective is the potential physical cleaning in removing a fouling layer from a ceramic NF membrane?*
3. *What is/are (an)other potential technique(s) to protect or remove fouling from the membrane surface?*
4. *How effective is/are the new technique(s) to protect or remove fouling from membrane surface?*
5. *How large are the costs and environmental impact of the successful methods during practical implementation for sewage water treatment?*

To accomplish the research objectives and answering the research questions, this research was further broken down into a series of structured steps:

1. Literature review

As the first step, a literature review that is shown in chapter 2 was conducted to understand the filtration process in ceramic NF membranes, the formation of fouling in sewer mining, and suitable methods that can be applied to remove membrane fouling.

2. Experimental design

The synthetic sewage water that will be used throughout the whole experiment is formulated based on the major foulant found in the literature research. Physical cleaning that has no potential in causing damage to the membrane and compatible with existing filtration set-up will further be studied. In case of secondary layer approach, materials that have already shown good performance as a coating layer and those which exhibits potential to triggers effective chemical reaction in removing fouling layer will also be investigated. All the setup and procedure can be seen in chapter 3.

3. Fouling control experiment

At this stage, the procedure as design in chapter 3 will be tested. Ceramic NF membrane filters the synthetic sewage water for 2 h. Cleaning was done in between the 2 h filtration. The permeability of membrane during the filtration process is monitored, thus cleaning recovery can be calculated. During the cleaning process, various parameter will be investigated to extract information how cleaning effectivity is changing towards shifting parameters. Chapter 4 shows phenomena that occur during the filtration due to the changing

of the parameter. Furthermore, the complete data of each experiment is shown in the appendix part of the report

4. Analysis

Finally, results of different fouling control methods will be compared in chapter 5, to obtain the best possible approach. Theoretical elaboration on larger scale operation is also conducted to analyze the impact and feasibility of implementation in the real sewage water filtration.

2 Background Theory

2.1. Membrane separation technology

In the water processing, the membrane acts as a very specific filter that will let water flow through, while it retains the suspended solids and other substances. Dirty water comes as a feed to the membrane and splits into two different streams after it passes the membrane surface. The first stream is called as the waste or concentrate that contains a lot of colloid and minerals. The second stream mainly consist of purer water and called as permeate.

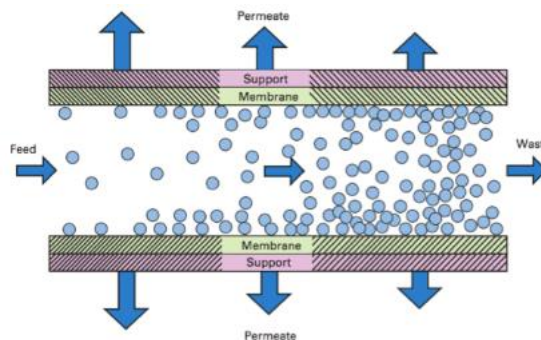


Figure 2.1. Illustration of tubular membrane filtration [8]

The membrane can be classified as microfiltration, ultrafiltration, nanofiltration and reversed osmosis based on their range of pore sizes. The following diagram shows the range of pore sizes, kind of compounds that can be rejected and common applied pressure for each class of membrane.

Size [μm]	0.001	0.01	0.1	1	10	100	1,000	P [bar]
Molecular weight [D]	100	200	1,000	10,000	20,000	100,000		
Compound type	Ions	Viruses	Humic acids	Bacteria	Algae	Cysts	Sand	
Membrane filtration type	Dissolved salts		Microfiltration	Clay	Silt			0.05
		Ultrafiltration						0.1
		Nanofiltration						5
	Reverse Osmosis							30

Figure 2.2. Membrane classification [9]

2.2. Nanofiltration & Ceramic membranes

2.2.1. Nanofiltration membrane

As indicated in Figure 2.2 nanofiltration membrane has a pore size that ranging from slightly lower than 0.001 to slightly above 0.01 micrometer. The natural organic matter which in Figure 2.2 Illustrated as humic acids, viruses, and dissolves salts can be retained by Nanofiltration membranes. Having molecular weight cut-off (MWCO) in range of 350-500 Da, NF membranes have been used widely in desalination, pharmaceutical, and surface water treatment [10].

2.2.2. Ceramic nanofiltration membrane

Conventionally nanofiltration membrane is made from polymeric materials. A lot of limitation arising from the polymeric nanofiltration membrane triggers new membrane development, that results in the discovery of a ceramic membrane. The ceramic membrane has higher chemical, thermal and mechanical stability compare to a polymeric membrane. As an example, a ceramic membrane can stand elevated temperature up to 500 degree Celsius and extreme pH range operating conditions between 1-14 [11]. The application of ceramic membrane can be found in gas-gas separation, petrochemical industry and acid or alkaline separation[12].

2.2.3. Ceramic membrane structures

Ceramic membrane may consist of several channels as illustrated in Figure 2.3 during filtration, water flow through each channel and with the help of pressure clean water will be filtered towards the channel's wall.

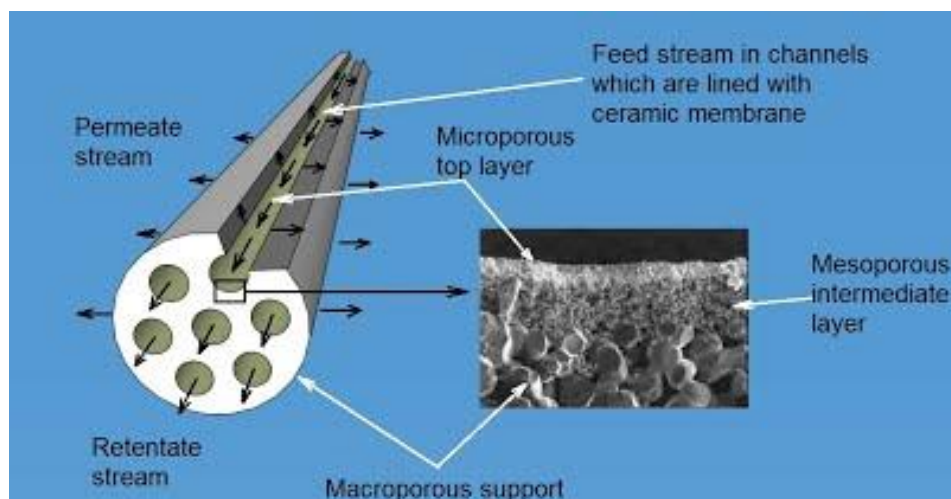


Figure 2.3. Ceramic membrane structures [13]

Ceramic membranes are made of several layers with different pore sizes. First, a support layer which commonly made from the metal oxide and other materials such as plasticizer and binder. Above the support layer is a mesoporous intermediate layer, followed by the top layer. The top layer was created by dip coating the support layer into a nanoparticles colloid. Altering the top

nanoparticle layer will produce a membrane with a specific desired property, which can improve the separation process.

2.2.4. Membrane flux and permeability

Membranes performance was usually defines based on its ability to produce clean water. It can be described through several terminologies such as flux and recovery. Flux is a measure of water flow rate over a certain area of membrane surface [14]. Most of the time the researcher defines flux calculation based on Darcy's law as [15]:

$$J = K_w \frac{TMP}{\mu} \quad (2.1)$$

Where,

J = flux ($m^3 / (m^2 \text{ s})$)

K_w = membrane water permeability ($m^3/m^2 \text{ s/Pa}$)

TMP = trans membrane pressure (Pa)

μ = absolute viscosity

Water viscosity in the equation above has to be adjusted based on water temperature, which was formulized by American Water Works Equation [16] as:

$$\mu_{(T \text{ } ^\circ C)} = \mu_{(20 \text{ } ^\circ C)} \exp^{-0.0239((T \text{ } ^\circ C)-20)} \quad (2.2)$$

Furthermore, if there is a cleaning action during the filtration process, membrane permeability as shown in equation 2.1 is used as a cleaning efficiency indicator. The effectiveness of the cleaning method usually defines as an ability to recover the permeability of the membrane to its initial condition [17]. This terms is called as permeability recovery which express as:

$$PR = \frac{K_{wc} - K_{wf}}{K_{wi} - K_{wf}} \times 100 \% \quad (2.3)$$

Where,

K_{wc} = membrane permeability after the cleaning ($L/m^2/h/bar$)

K_{wf} = membrane permeability of the fouled membrane ($L/m^2/h/bar$)

K_{wi} = initial membrane permeability before the cleaning started ($L/m^2/h/bar$)

2.3. Fouling in membrane filtration

2.3.1. Fouling mechanism

There are four mechanisms in which membrane can be fouled. First, complete blocking occurs when the colloidal particle has a size that identical to the membrane pores, thus completely closed the membrane pores. Second, standard pore blocking which occurs when foulant deposit on the

channel of membrane pores and cause filtration flux to decrease proportionally with the volume of deposit materials that fill the membrane channel. Third cake filtration, particles do not interact with the clean water passage, Instead it deposits on the membrane surface and eventually forms a fouling layer as described in Figure 2.4 (c), where another foulant can also stick to it. Fourth, the intermediate blocking which is a combination of cake filtration (foulant stick to other particles) and pores blocking. The illustration of a membrane blocking mechanism is illustrated in Figure 2.4

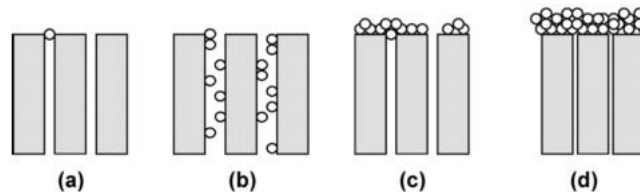


Figure 2.4. Membrane fouling mechanism: a: complete blocking, b: intermediate blocking, c: cake filtration, and d: intermediate blocking [18]

These fouling layers could also be further differentiated as reversible and irreversible types, based on how the membrane can be cleaned. Reversible fouling mostly occurs due to the cake layer or concentration polarization on the membrane surface and can be removed using physical cleaning methods such as backwashing, forward flush, and other hydrodynamic process. Meanwhile, non-reversible fouling caused by deposition of the material inside the pore of the membrane which further leads to membrane blockage. Since most of the physical cleaning cannot affect to the fouling inside the membrane pores, the non-reversible fouling is more effectively removed by chemical cleaning[19].

2.3.2. Foulant

Raw water has several constituents that can cause fouling. Materials which can cause fouling and blockage on the membrane surface is classified as foulant. The following are major foulant on water treatment process [20]:

- **Particulates**

Particulates fouling can lead to complete blocking of the membrane pores and is usually arises from continuous deposition of colloidal particles [21]. Materials such as colloids suspended solid, and organics can fall into this classification. This broad classification leads to algae, bacteria, and NOM also categorized as particulates [22]. However, in membrane separation particulates fouling usually refers to particles that are biologically inert.

- **Organic**

Organic fouling in membrane separation associated with bulk organic matter (OM). The concept of organic foulant in membrane separation process can easily be misunderstood since it can include organic colloids and microbiological organism[23]. The biotic form of

organic colloids, which its cellular activities create fouling will further be classified as biological fouling (microbiological organism). On the other hand, the abiotic form such as molecular debris refers to organic fouling.

- Inorganics

Inorganics fouling caused by deposition of salts on the membrane surface when the concentration of a particular salt in solution exceeds its saturation point during the filtration operation[24]. Blocking mechanism of inorganic salts can be through concentration polarization, cake or gel layer formation, or membrane pore blocking[25].

- Microbiological organism

Microbial fouling refers to the fouling that is caused by microbial activities on the membrane surface. As part of their metabolism process microbes produce chemicals such as extra polymeric substrates that can contribute to blocking membrane pores. The degree of the fouling is highly dependent on the types of microbes present in the water and the chemicals produced. Most of the time bacteria which growth on the membrane surface form a cluster, in which the bacterial activities of one species is affecting the others. Such interdependencies usually result in biofilm formation [26]. In general, the biofilm is a strong fouling layer, which cannot be easily removed by the physical process[27].

2.3.3. Fouling in sewer water filtration

In treating surface water, it has been identified by Kimura [28] that one of the major components of foulant is extra polymeric substances (EPS). EPS is naturally occurring polymers that have high molecular weight. Humic substances, proteins, polysaccharides, nucleic acids, lipids are a common example of EPS in surface water.

Another research done by Ran [29] shows that biopolymers triggers the blockage of membrane pores and lead to irreversible fouling formation. The same research mentions that pore blocking, and formation of a strong cake layer is the main mechanism in which irreversible fouling was formed. However, different membranes have a different preference of mechanism in which the irreversible fouling developed. A membrane with bigger pore size is more susceptible to pore constriction, while in the smaller pore size membrane irreversible fouling can be caused by cake layer formation.

In ceramic NF sewer mining process, the formation of dense cake layer has been identified as a major contributor to fouling. Cake layer is usually formed by sodium alginate in water [30]. Alginate can have interaction with other ions such as calcium. Calcium ion will serve as a bridge that connects several alginate molecules and forms an egg-box structure [31]. This structure will further be responsible in the formation of a gel layer on the membrane surface. Gel layer formation starts during the water filtration process, in which the first alginate layer stick on the membrane

surface. The presence of calcium ions then will add a new layer of alginate to the previously formed layer, thus leads to cake layer formation. High pressure during the filtration process will densify the cake layer structure and transform it into a strong gel layer.

2.4. Membrane cleaning

As the fouling is building up on the membrane surface, cleaning then need to be performed regularly. Usually, several physical cleanings will be done first to dislodge and remove foulant from the membrane surface. As the filtration process continues for a certain period, a large accumulation of irreversible fouling will take place. At this point, chemical cleaning will be conducted to weaken the cohesion and adhesion force between the foulant and membrane surface.

Physical cleaning utilizes the shear stress or pressure difference to remove the foulant from the membrane surface, while chemical cleaning relies on the chemical agent to trigger a reaction with the foulant. Another means to achieve optimum fouling control is by using fouling prevention strategy. This can be done by covering the membrane surface with an additional layer which has more hydrophilic properties to prevent the adhesion of foulant on the membrane surface or can trigger a reaction that degrades the foulant. In the proceeding section summary of some methods for physical, chemical cleaning, and fouling prevention will be discussed.

2.4.1. Physical Cleaning

Physical cleaning method utilizes mechanical force to remove the foulant that is attached to the membrane surface [32]. Physical cleaning comprises of many techniques. In the following section, common methods such as backwash and reverse flush to the latest application of water hammer and sonification will be further explained.

Forward and Reverse Flush

The operation of the forward flush is similar to normal filtration mechanism. However, the applied pressure will be less, and flux will be much higher. It was found that high-pressure hydraulic cleaning results in lower flux recovery [33]. The same report stated that the best hydraulic cleanliness achieved when the transmembrane pressure (TMP) around zero, since lower TMP prevent re-depositing of foulant. In the most cases, forward flush was conducted by using the feed water to minimize the clean water loss [34]. In some operation, the direction of forward flush from feed to concentrate is changing periodically from concentrate to feed, this operation is called as reverse flushing. The following figure illustrates forward, and reverse flush mechanism:

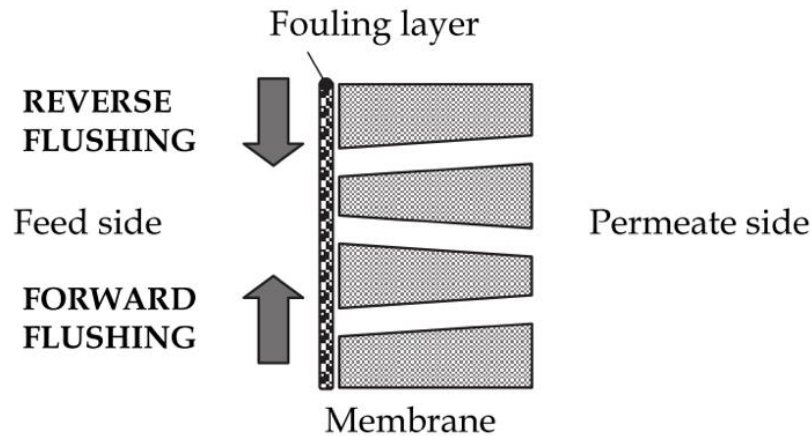


Figure 2.5. Forward and reverse flushing [32]

Research on ultrafiltration membrane with limed sugarcane juice shows that intensive hydraulic cleaning (e.g., rinsing with tap water) can recover 18 to 25 % of initial membrane flux [5]. In the other experiment where ceramic membrane was utilized to remove sodium alginate from feed stream 50 % of initial flux can be achieved solely by rinsing the membrane thoroughly with ultrapure water [30]. In that experiment, cleaning was performed after membrane reaches 70 % reduction of its initial flux.

Furthermore, the effect of the cross-flow velocity during cleaning process highly depends on the types of foulant. Earlier it was believed that crossflow velocity provides an additional shear force to break the fouling layer and also reducing concentration polarization and taking away the colloidal particle from the membrane surface [35]. In contrary, other experiments on ultrafiltration ceramic membrane prove that rinsing ceramic membrane (mimicking hydraulic cleaning) with flow velocity between 2-6 m/s doesn't have any effect on cleaning efficiency [36].

Backwash

Backwash is an opposite mechanism of the normal filtration process. In backwash, the water flow is reversed. Clean water from permeate side will be pumped back to the feed side. Thus the pores of the membranes are flushed inside out. During the backward process, the pressure of the membrane in the permeate side is also set greater than in feed side.

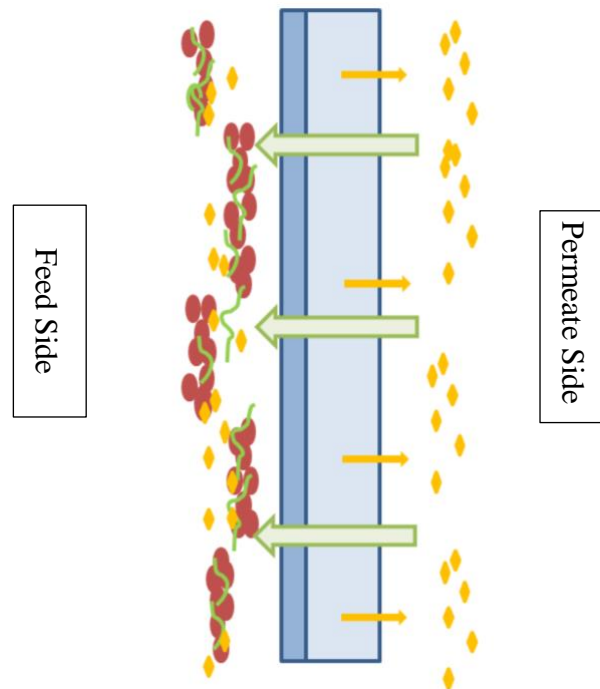


Figure 2.6. Water flow during the backwash process [37]

Backflow from the permeate to the feed side help to expands the fouling layer and make it more relax. In some cases, the backflow can directly fluidize and removed the foulant from membrane pores. Backwash is often combined with a forward flush to enhance the cleaning effect. After the foulant has been fluidized from the membrane pores, the forward flush is applied to completely detached the fouling layer [32]

The application of the backwash flush has shown a great achievement in terms of cleaning efficiency for polymeric ultrafiltration. Some research shows that the flux recovery can reach 100 % recovery. Application of backwash into Ultrafiltration hollow-fibre membrane module to remove the gel layer produced as a result of Ca^{2+} interaction with alginate ion shows flux recovery of 100 %. In that research 2 mM of Ca^{2+} was used and duration of filtration and backflush last for 1 hour and 5 minutes respectively [31].

Another success story of the backwash application on the ceramic ultrafiltration membrane to remove zeolite cake shows that short and frequent backwash can retain initial membrane flux. The following diagram shows the result of the research.

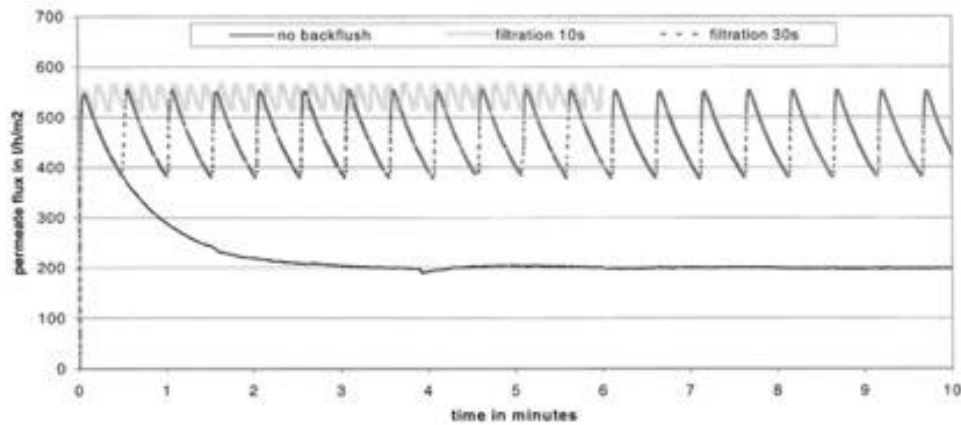


Figure 2.7. Permeability profile of frequent backwash [38]

In this experiment backwash was performed in 0.2 s with different filtration time. The trans membrane pressure during the backflush process was not very high. The optimum TMP during the whole experiment was found about 2 bars. This pressure is not very high and sufficient enough to reduce the fouling. In the end, the same paper also indicates the success of this process highly dependent on the types of foulant [38].

However, the successful application on ultrafiltration membrane cannot be reproduced in ceramic nanofiltration membrane cleaning using sodium alginate as foulant. Investigation of backflush on ceramic nanofiltration membrane lead to deterioration of membrane surface [39]. The glass tip parts of the ceramic nanofiltration membrane in cross-flow set up ruptured after backwashed with 5 bar pressures.

Water hammer

Further improvement in membrane cleaning process aims for a method that reduces the permeate water consumption during the cleaning process. One of the most promising methods was the utilization of water hammer phenomena performed by Broens et al. [40]. His concept stress on dynamically altering the filtration process, as an example through oscillatory flow and vibrating the membrane. The novelty of his research mainly emphasized on stopping the water flow to alter the whole filtration process by shutting off the valve in the permeate site. This action leads to fast pressure fluctuation which called as water hammer phenomenon.

During the experiment after each 15 to 20 s of the filtration process, the permeate valve will close for 0.75 to 5 s. This sudden closing process can generate a pressure fluctuation of 0.05 to 0.1 bar. By applying water hammer method, membrane life time before the chemical process needed can be extended significantly. However, water hammer method can only be effective if it's performing above critical flux. Working above critical flux has a drawback of faster foulant deposition. In the end, the effectivity of water hammer is a combination of its cleaning effectivity and faster fouling process on the membrane surface.

Ultrasound

Ultrasound cleaning needs to be coupled with backflush or forward flush. This idea is arising to limit the number of frequency in which chemical cleaning needs to be performed [41]. There are several alternatives in which the ultrasound can be applied to the membrane: with moving ultrasound transducer or fix transducer but with moving membranes. Sonication supplies sufficient vibrational energy to keep the foulant suspended in the water. In this process, ultrasound keeps the foulant away from the membrane surface [42].

In the experiment conducted by Boley et al. [41] ultrasound was able to manage higher flux through the whole filtration process. Application of pulse and continuous ultrasound has an average flux of 2 and 2.5 times higher respectively, compares to filtration without any treatment.

This system was used to treat creek water which contained 9 mg/L of humic acid. The membrane used for the whole process was ultrafiltration ceramic membrane that equipped with an ultrasonic transducer. The ultrasonic transducer will move back and forth along the membrane module as a filtration process occurs. Despite its promising result, ultrasound membrane has a drawback in which it damages the membrane surface, which results in the permeate cross contamination after 20 days of operation [41].

2.4.2. Chemical Cleaning

When physical cleaning is not effective, chemical cleaning can't be avoided anymore. Choice of chemical agent and operating condition is critical for chemical cleaning effectiveness. Chemical cleaning most of the time performed under low trans membrane pressure to relaxed the compressed fouling layer [41].

Furthermore, the optimal option of chemical agent has to be able to dissolve most of the deposited material and at the same time giving less damage to the membrane surface. The list of fouling type and chemical agent as summarized by Fritzmann et al. [43] shown in the Table 2.1.

Table 2.1. list of fouling type and chemical agent [43]

Type of fouling	Chemical agent
Colloidal	NaOH solutions, chelating agents, and surfactants
Organic	NaOH solutions, chelating agents, and surfactants
Metal oxides	Citric acid with low pH or $\text{Na}_2\text{S}_2\text{O}_4$
Silica	NaOH solutions with high pH
Carbonate scales (CaCO_3)	Citric acid or HCl with low pH
Sulphate scales	HCl solutions or sequestration agents (EDTA)
Biofilms	NaOH solutions, chelating or sequestration agents, surfactants and disinfectants

Caustic

Caustic is effective to remove the natural organic matter, by means of hydrolysis and solubility [44]. Polysaccharides and proteins are an example of organic foulant that can easily be removed by caustic solution. However, hydrolysis can also be dangerous to some membranes. As an example, the cellulose based membrane can easily be hydrolyzed by the caustic solution.

Solubility can occur since at high pH hydrogen in natural organic molecules will easily be dissociated, thus leaving NOM negatively charged. This negative charged NOM, increase its hydrophilicity which results in dissolution of a NOM in the water. Some lipids could also be removed by a caustic solution such as NaOH through saponification reaction.

Acids and chelating agent

A lot of inorganic fouling is more soluble in an acidic environment. Even though acid solution will not be able to dissolve inorganic fouling completely, it would be sufficient to let the rest of the fouling layer become backwash-able. Acids such as Hydrochloric acid are widely used to clean inorganic fouling. However hydrogen fluoride and sulfuric acid can be harmful since they can damage the membrane and promotes precipitation of sulphate salts. Another acid such as citric acid can also work as a chelating agent, by reacting with inorganic and forming a stable water-soluble complex [32].

Surfactants

Surfactants refer to a compound that has both hydrophobic and hydrophilic end. This molecule will act as a connector between hydrophobic foulant and water. The hydrophobic end of surfactant will attach to the foulant, and the hydrophilic tail will help to dissolve surfactant-foulant complex

to water. Some surfactants can form a micelle structure with fat and oil [44]. One of the most known surfactants is detergent. Application surfactant on removing protein fouling on polymeric ultrafiltration membrane has been showing great effect, however, insufficient cleaning could lead to the formation of micelle cake from surfactant residue, which results in flux decline [45].

Oxidants

Among all of the chemical agents when treating surface water or specifically dealing with natural organic matter (NOM), an oxidative agent such as sodium hypochlorite and hydrogen peroxide has been proven to be very effective. NOM removal efficiency of sodium hypochlorite and hydrogen peroxides are 87 % and 28 % respectively. These values are higher than the performance of hydrochloric acid with 23 % removal and sodium hydroxide with only 9 % removal [46].

Another example of the oxidation agent is ozone. Ozone is one of the solutions that give good removal when it reacts with NOM present in the water. Investigation of ozone performance has been done by Suhartono and Khayrullina [7], [47]. In their research ozone cleaning was applied on polyvinylidene fluoride (PVDF) membrane to remove NOM fouling. Several cleaning durations was applied on the membrane surface. The best outcomes were achieved using 3 mg/L ozone solution in 10 min cleaning duration. Highest removal of NOM layer on the membrane surface was 82 %. The filtration process was performed with a TMP of 3.85 bar and a pH of 7.

2.5. Fouling Prevention

The fouling prevention refers to an action that turns the membrane surface to become less susceptible to the fouling. This is done by coating the membrane with the anti-fouling extra layer. This layer will have a property that reduces the adhesion potential between the foulant and membrane surface [48].

One of the fouling prevention method is enhance pre-coat engineering (EPCE) which was introduced by Galjaard, et al. [50]. The precoating is done by flowing particle suspension on the membrane for a short period. These particles then form a removable layer in which the foulant will stick on it. After a certain filtration period, backwash will remove both coating and fouling layer altogether. Precoating is performed after each backwashed cycle. Some materials such as Ferrous (II) oxide, PAC, Iron (III) chloride, titanium oxide, zeolite, diatomite, kaolinite, and bentonite have already been proved as an effective coating agent.

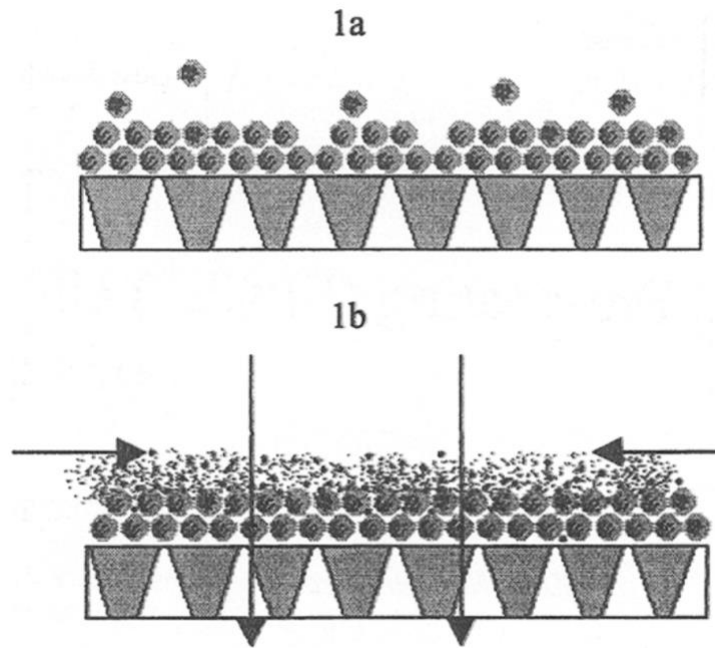
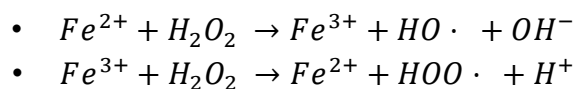


Figure 2.8. EPCE Complete Filtration Process (1a: Coating solution deposition on membrane surface; 1b: foulant deposition on the secondary layer)[51]

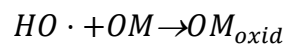
EPCE methods can't be used on ceramic nanofiltration membrane due to its dependency on backwash; however, the materials chosen for the secondary layer can be reacted with other chemicals to release it from the membrane surface. In the following subsection, some of the potential chemical reactions will be further discussed.

2.5.1. Fenton reaction

In particular, material such as Iron is widely known as a catalyst for hydrogen peroxide advance oxidation which called as Fenton reaction. In this reaction, iron will act as a catalyst to produce free radicals which further will reacts and degrades the NOM. The following reaction was proposed by Pignatelo et al. [52], as a mechanism to produce hydroxyl nanoparticles.



After that produced hydroxyl reacts with the organic matter according to the following reaction:

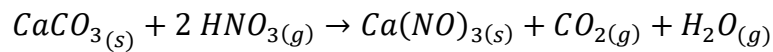


Some applications of Fenton reaction on ceramic membrane filtration has been studied by de Angelis [30] on ultrafiltration membrane. During the experiment, the ferrous oxide nanoparticles are produced and sintered so they can strongly attach to the membrane surface. The results are showing that the cleaning process of Fenton degradation worked best at a pH of 2.5 to 3. Furthermore, the experiment has been reported to achieve stable flux recovery of more than 80 % for all the organic foulant that was tested.

Based on the research mentioned above, Fenton reaction provides an opportunity for the cleaning process to be more effective. Especially for nanofiltration ceramic membrane where backwash cleaning is avoided. However, further investigation of a method and optimum condition to attach iron (II) ions needs to be investigated.

2.5.2. Calcium Carbonate

Another possible chemical reaction to improve the efficiency of the membrane is the reaction of calcium carbonate with a weak acid. Calcium carbonate solution has been widely applied in environmental science as a filter to reduce air pollution from the air. One of the laboratory studies has been done by Goodman et al. [53], to observe the heterogeneous reaction between calcium carbonate particles nitric acid. The following reaction has been proposed:



During the investigation, it was observed that the surface of calcium carbonate particles evolved as the reaction took place and can reduce the acid concentration by 70 to 80 % of its initial concentration. Other experiments involve calcium carbonate, and formic acid was done by Usher et al [54] and Al-Hosney et al. [55] in which the last mentioned experiment can reduce formic acid concentration up to 91 %. There is a similarity over all of the experiment in which all the reaction will have higher conversion as the nanoparticle relative humidity increases. Therefore, these values can give an indication that acid can be used as a solution to remove $CaCO_3$ layer that covers ceramic nanofiltration membrane.

3 Materials and Methods

3.1. Materials

Techniques that can remove the fouling without causing any damage to the membrane surface such as forward flushing, coating with iron, and calcium carbonate were tested in the experiments. The following are the materials required to perform the experiments and their preparation process.

3.1.1. Sewage water preparation

Instead of using real sewage water which has inconsistent quality (seasonal effect and location can affect sewage water quality), in this research synthetic sewage water was used. Synthetic sewage water can be easily reproduced for each run of the experiment, and the results become more comparable to one and another.

As mentioned in the previous chapter, one of the primary constituents that lead to fouling formation is sodium alginate. Therefore, sodium alginate is added to demineralized water to simulate the sewage water. In total 30 L of synthetic sewage water was used for each filtration experiment. The sodium alginate solution was first stored in the refrigerator at 12-14 °C to avoid bacterial contamination. Furthermore, the solution needed to be stirred continuously to make sure that the sodium alginate powder completely dissolved. Salts such as NaCl, CaCl₂, and NaHCO₃ were also added to the synthetic sewage water to provide buffering properties and triggering the formation of gel layers from alginate-calcium interaction. Table 3.1 shows the concentration of each constituent added to the synthetic sewage water.

Table 3.1. Synthetic sewage water specification

Compounds/Parameters	Units	Values
Sodium alginate	g/L	0.8
NaHCO ₃	mM	1
NaCl	mM	5
CaCl ₂	mM	3
Conductivity	mS/cm	1400 ± 200
pH	-	7 ± 0.5

3.1.2. Iron hydroxide solution

Iron (III) chloride 41% solution from Merck was used as an iron source for coating solution. The stock solution of iron chloride was kept at a pH of 2, to avoid the oxidation or reduction of iron. Iron chloride coating solution was prepared by adding stock solution into 10 L of demineralized

water. Amount of stock solution that is added to demineralized water will be adjusted to investigate the effect of iron concentration. Furthermore, pH of dosing solution is adjusted to 5, 7 and 8, as different pH will result in the different size of iron flocs. The coating solution was agitated continuously during the coating process.

3.1.3. Iron oxide nanoparticles

Iron oxide (Fe_3O_4) powder from Sigma Aldrich was used to formulate an iron oxide coating solution. Iron powder was in nano powder form with the size distribution between 50 to 100 nm in 97% of trace metal basis. Both iron (II) and iron (III) ions are present in the iron nanoparticle thus providing a chance of having both Fenton and Fenton-like reaction. Iron hydroxide powder is also added to demineralized water at a pH of 2 since iron hydroxide nano particles can only be dispersed in low pH [56]. The coating solution was stirred continuously during the coating process.

3.1.5. CaCO_3 solution

Calcium carbonate solution was prepared from CaCO_3 powder produced by Merck. CaCO_3 powder was mixed with water to make a colloid solution. It is important to make sure that there is only a little CaCO_3 that dissolve into Ca^{2+} and CO_3^{2-} to provide as much CaCO_3 as possible for the regeneration reaction, for that reason the pH of the solution set to be on the point of zero charge which is 10 [57]. After that, to ensure CaCO_3 particles are uniformly distributed in the solution, 3 hours of sonification with 40 % amplitude was performed [58]. The supernatant of this solution then taken and used as a feed solution.

3.1.4. Membrane Characteristic

In this experiment, ceramic nanofiltration membranes produced by Inopor GmbH were used. This C-NF membrane was made from TiO_2 for the coating layer and AlO_3 for the support layer. The complete specification of the membrane can be seen in the Table 3.2.

Table 3.2. Specification of INOPOR EKR membrane

Parameter	Value
Outer diameter	10 mm
Channel diameter	7.0 mm
Number of channels	1
Specific membrane area	0.001627 m^2/m
Membrane area at 1200 mm length	0.001953 m^2



Figure 3.1. Inopor EKR ceramic nanofiltration membrane

3.1.5 Experimental set-up

The complete set-up for the whole experiment is shown in Figure 3.2. The entire set up consists of: Feed tank, feed pump, coating solution tank, dosing pump, membrane installation and computers to run the OSMO set-up and record the permeability data.

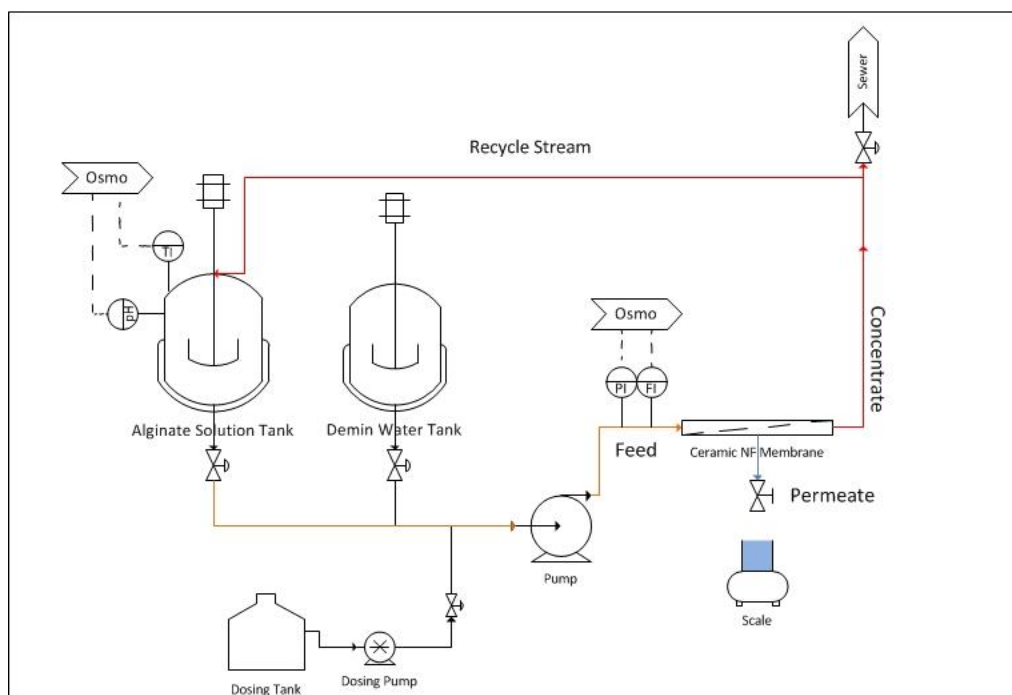


Figure 3.2. Filtration set-up

The whole filtration set-up was operated through a computer with Osmo inspector software (Convergence B.V.) that allows the user to control filtration parameters such as flow rate and pressure. The permeability of the membrane throughout the filtration time was calculated based

on the increase in permeate weight during the filtration time that is measured by a scale connected to the main computer.

3.2. Methods

The effectiveness of each cleaning procedure can be compared by determining the permeability recovery after each cleaning method. Recovery can be calculated by constantly monitoring permeability of ceramic nanofiltration under constant pressure filtration for both forward flush and coating experiments. As the filtration process goes further, foulants will be deposited that leads to permeability drop of the ceramic NF membrane. At a certain point the membrane cleaning process, which in this case are forward flush, Fenton or acid-calcium carbonate reaction, will take place to release the foulants from the membrane surface. An indication of fouling layer removal is the rising of permeability.

Every filtration experiment starts with a clean water permeability test. 1.1 m/s demineralized water produced in TU Delft water lab flows through the membrane at a TMP of 3 bar. This filtration last for 1 h to make sure the membrane is clean and there is no defect on its surface. During the process permeability was recorded every second. Precoating experiment consisted of 2 coatings, 3 filtrations and 2 cleanings. Experiment to test the effectivity of precoating method started with the membrane coating process, followed by first filtration and cleaning. After the first cleaning, membrane was ready for another coating process and the whole sequence was repeated until it stopped in the third filtration. The following explains the procedure in operating and monitoring the permeability of the fouling control measures.

3.2.1. Forward flush investigation

The fouling experiment uses 30 L of synthetic sewage water which was pumped through the membrane at 1.1 m/s cross flow velocity and a TMP of 5 bar. Membrane rejects were then recycled to the feed tank. The solution in the feed tank was stirred continuously to ensure the homogeneity of the feed solution. The filtration period was varied to investigate the effect of cleaning interval on forward flush effectivity.

After the fouling took place, at a certain period the forward flush can be started by releasing the pressure. Releasing the pressure leads to cake relaxation which makes the fouling layer easier to be removed. Total filtration time was 2 h, with various forward flush cross flow velocity, cleaning duration, cleaning water flow and sewage water filtration.

3.2.2. Iron coating experiment

The coating process started by mixing the dosing solution to the demineralized water stream. The coating solution was pumped through a dosing pump to the mainstream of the OSMO inspector pump.

During the coating process TMP was set to 5 bar with 0.4 m/s cross flow velocity. The low flow was chosen to ensure iron molecules to be deposited on the membrane surface by keeping the feed in laminar regime. The whole coating process lasted for 10 min. During the coating, iron content of the feed, permeate and reject streams was also checked with total iron test kit (Merck), this value was further used to calculate the amount of iron deposit on the membrane surface.

After the coating was done, filtration took place. Alginate filtration was set at 1.1 m/s cross flow velocity and 5 bar pressure. After a certain filtration period, filtration is stopped, and the membrane was removed from the set-up and put into a hydrogen peroxide solution for regeneration. The pH of the peroxide solution was around 2.5 since this is the optimum pH of Fenton and Fenton-like reactions [59]. Once the cleaning finished, the membrane was put back into the filtration set-up, and it underwent another coating process before another filtration of alginate solution took place. In some experiments, after the membrane cleaning, and before coating process is performed, forward flush with 3 m/s cross-flow flow was done for 5 min to wipe all the loosened cake from membrane surface to gain better filtration recovery. The cleaning duration, cleaning interval and dosing concentration was varied during the iron coating experiments.

3.2.3. CaCO_3 coating experiment

The CaCO_3 solution that was created by sonication was poured into the dosing tank. From the dosing tank, the CaCO_3 solution was transferred to the main stream by the dosing pump. In the mainstream the CaCO_3 solution was mixed with demineralized water, and eventually reaching the membrane. The pH of the mixture of the CaCO_3 solution with demineralized water was monitored and kept always around 10 to avoid CaCO_3 dissolution. During the coating process the pressure of the main pump was set to 5 bars with 0.4 m/s flow.

The fouling experiment was then started after CaCO_3 coating was finished. 1.1 m/s alginate solution was filtered through the membrane at 5 bar pressures. At a certain period of filtration, the membrane was removed from the housing to undergo the cleaning process by dipping membrane in an acidic solution. After each cleaning process, the CaCO_3 coating was repeated to replace the old layer of coating that was removed by the reaction between acid and calcium carbonate.

3.2.4. Chemical cleaning

At the end of every filtration experiment, the membrane was soaked in a 0.1% sodium hypochlorite solution to remove the organic fouling layer completely. The membrane was immersed for 1 h in sodium hypochlorite solution and then followed by 30 min flushing with 0.67 m/s demineralized water to completely wash the sodium hypochlorite from the membrane surface and carry away the remaining debris. In the coating experiment with iron chloride layer, the membrane was dipped in the 400 mg/l citric acid solution before the sodium hypochlorite for complete detachment of the remaining iron oxide.

4 Experimental Results and Discussion

4.1. Forward flush investigation

The experiment of forward flush has investigated the effect of cross-flow velocity, duration, and interval on recovering the permeability of the membrane. The first part of the investigation, the cross-flow velocity, which partly was performed by Wantz [60], see section 4.1.1. The investigation on the duration of forward flush and the time interval in which forward flush was performed are shown in the section 4.1.2 and 4.1.3 respectively.

4.1.1. Effect of cross flow velocity

Forward flush was performed under 4 different cross-flow velocities (0.4 m/s, 1.1 m/s, 2.2 m/s, and 4.3 m/s). Cleaning was conducted after 20 minutes of synthetic sewage water filtration. The result is depicted in the Figure 4.1:

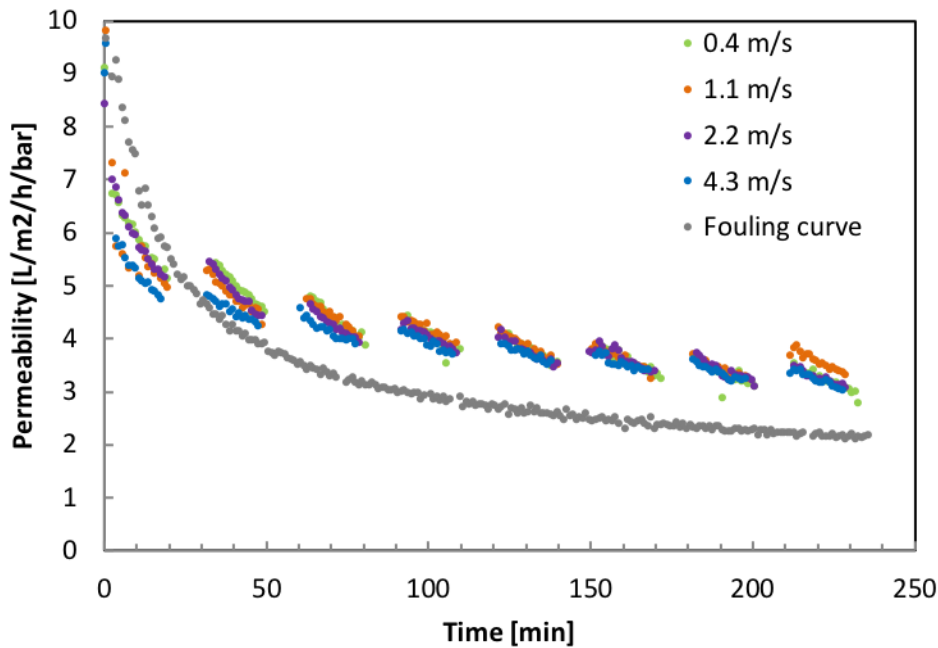


Figure 4.1. Effect of cross flow velocity on membrane permeability

The Figure 4.1 shows in the case of alginate fouling on ceramic nanofiltration membrane, the increase in cross-flow velocity has small effect on membrane permeability. However, performing forward flush gives higher permeability in the long period of filtration than the filtration without forward flush.

This phenomenon is contradictory to other researches that are focus on investigating the effect of cross-flow velocity on the membrane [61] ,[62], [63]. Higher cross flow velocity should contributes to higher shear stress and on the membrane surface. Thus, reducing particle attachment on the membrane surface and creating back transport of molecules from the membrane surface[64].

However, in case of sodium alginate filtration the fouling mechanism started with pore constriction [65]. The higher shear stress on the membrane surface due to higher cross flow velocity will have less impact on the fouling inside the membrane pores.

4.1.2. Effect of forward flush duration

Four different forward flush durations, 1, 3, 5, and 10 minutes, were investigated during the experiment to determine the minimum duration required to remove the reversible fouling. The filtration and forward flush cross flow velocity was 1.1 m/s with TMP of 5 bar. During the forward flush, feed water cross flow velocity was kept at 1.1 m/s and the pressure was released to make the fouling layer more relaxed and easier to remove. The complete permeability curve of the investigation on forward flush duration can be found in the Figure A1 of Appendix A.

The results show that 3, 5 and 10 min forward flush attained a 33 % higher permeability compared to the condition where forward flush was absent. However, 1 min forward flush was not effective in removing the alginate fouling layer since it followed the same pattern of permeability curve as when there was no cleaning effort made.

4.1.3. Effect of cleaning interval

Based on all the experiments on forward flush that has been carried out, the sharp decline in water permeability occurred during the first 30 min, and afterward, the membrane gave a more stable permeability until it reached the end of the filtration time. Therefore, it was critical to disrupting the formation of the alginate layer in this period. One of the efforts to do that was by applying a shorter cleaning interval during the filtration.

To study the effect of cleaning interval 3, 5, 10 and 20 minutes cleaning interval with 5 minutes cleaning duration were tested. The permeability curves as shown in Figure A3 of Appendix A suggests that shorter cleaning interval results in the higher end permeability.

Regardless of higher permeability given by shorter cleaning interval, each cleaning interval, having different total filtration time. Therefore, it is necessary to check the results of shorter cleaning intervals by comparing their water production in 2 h. The result is depicted in figure 4.2

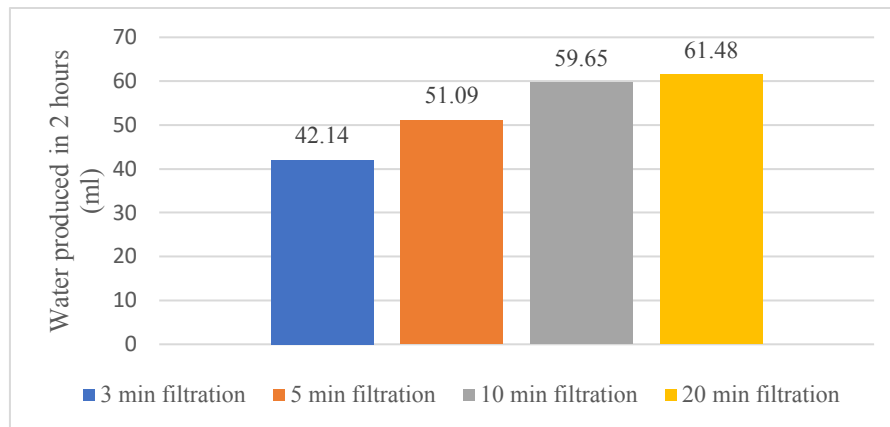


Figure 4.2. Water productivity of 3, 5, 10 and 20 minutes cleaning interval with 5 minutes cleaning duration

The highest water production is given by 20 min cleaning interval while the lowest given by 3 min filtration. Figure 4.2 implies that a shorter cleaning interval did not contribute to a better filtration performance. The membrane water production system with less cleaning frequency is thus more effective [35] due to the less down time, which leads to more clean water produced. Therefore, it can be concluded that the effort to disrupting the early fouling formation by shorter interval of forward flush was not successful.

As explained by another research, a steep decline in permeability at the beginning of filtration is caused by the loading effect [66]. Loading effect is a direct interaction between the membrane surface and the alginate molecules that creates firm fouling layer. This interaction mostly dominated by adsorption of foulant to the membrane surface which will lead to the pore constriction [31], that is hardly remove by forward flush.

As filtration of the alginate continues, the membrane's surface area that is available as a binding site for alginate will be diminished thus promoting more interaction between new alginate molecule that enters the membrane with a layer that already forms during the early filtration. The presence of calcium ions also enhances this new interaction.

This secondary layer is weaker than the first interaction where the alginate molecule attaches directly onto the membrane surface. The secondary layer can be removed by employing relaxation and mechanical cleaning [67], which explains why the forward flush is more effective in later stage of the filtration. However, at high pressure, the alginate gel layer can be compacted and less reversible [65]. Thus, the presence of calcium ions in alginate-alginate interaction with pressure applied to the filtration process dictate the effectiveness of forward flush.

4.2. Iron hydroxide coating

Parameters such as dosing concentration, pH of the feed solution, cleaning duration, cleaning interval and its combination with forward flush were investigated. The outcome of these experiments can be seen in subchapter 4.2.2 to 4.2.6. Before all the experiments above were

conducted, the comparison between the effect of Fenton-like reaction using iron hydroxide as a coating layer to the blank experiment was done and discussed in section 4.2.1.

4.2.1. Iron hydroxide Fenton-like reaction vs. blank experiment

The comparison with blank experiments is vital to ensure that an increase in membrane recovery could be a result of Fenton-like reactions instead of just an interaction between fouling layer with hydrogen peroxide. The blank comparison can also indicate if the iron hydroxide coating layer enhances more attachment of the foulant onto the membrane surface. Three different blank experiments were conducted, which were: iron hydroxide coating without any cleaning, hydrogen peroxide cleaning without iron chloride coating, and filtration without any treatment. The permeability curves of these blank experiments and filtration with iron hydroxide coating and hydrogen peroxide cleaning can be found in Figure B1 of Appendix B.

The condition where iron was coated to the membrane exhibits a lower end permeability value than when it was absent. Additional alginate attachment to the surface of the membranes can be explained by looking into the iron-alginate interaction. Iron performs the same function as calcium ions, in which they form a bridge to connect with the alginate molecules [68]. Based on this set of the experiments, the highest recovery can be achieved when both iron coating and hydrogen peroxide cleaning were both performed.

4.2.2. Effect of different dosing concentration

4200, 2100, 432 and 42 mg/l of iron hydroxide dosing concentration were tested to find the minimum concentration that can still promote the Fenton-like reaction. Permeability curve of each dosing concentration can be seen in Figure B2 in Appendix B, and the measured amount of iron in the feed stream and iron deposited on the surface can be seen in the Table B1 in Appendix B.

Similar permeability curves were given by 4200, 2100 and 432 mg/l iron hydroxide dosing concentration. However, 42 mg/l feed concentration failed to give a considerable permeability recovery since there was no iron coated on the membrane surface as shown in the Table B1 of Appendix B. The results of the dosing experiments suggest that there is no big difference in the permeability recovery once the minimum dosing has been exceeded.

4.2.3. Effect of feed stream pH

The pH is essential for the formation of iron flocs, in which it affects the size and strength of the floc. As iron (III) chloride dissolves in water, the molecules will undergo a hydrolysis reaction. Iron ions tend to form a new complex structure, in which water will act as a ligand. The presence of acids and bases on the solution will replace the water position as a ligand in that structure, promoting the formation of various types of iron hydroxide [69].

Iron hydroxide as the hydrolysis product is what later seen as yellowish flocs in the water. The pH dictates which iron hydroxide products will be formed [70]. The research on the iron floc state that it has the largest size at pH of 5 and decrease in size as it goes to pH of 7. However, once the pH of 7 has been passed the floc diameter will start to increase again and reach a stable size as the pH further increase [71].

Based on the information about the floc size and strength, the coating process for different iron chloride pH was investigated. 400 mg/l iron hydroxide with pH of 5, 7 and 8 were chosen to observe the effect of different floc size. Recovery of every cleaning can be seen in the Table 4.1 and Figure B3 of Appendix B for the complete permeability curves of the pH investigation.

Table 4.1. Permeability recovery by Fenton-like reaction at different pH

Recovery (%)	pH		
	5	7	8
First cleaning	49	68	53
Second cleaning	17	23	11

In accordance to the Table 4.1, at pH 7 the iron hydroxide coating shows a higher permeability recovery for both first and the second cleaning with 400 mg/l hydrogen peroxide. The pH of 7 produced smaller particles than other tested pH, which confirms that the smaller particles will promote Fenton-like reactions better. Tiny particles/flocs tend to distribute uniformly, thus providing good surface coverage and gives larger surface area exposed to the reaction.

4.2.4. Effect of cleaning duration

A system with high water productivity has only a small duration in which the membrane is not working. To achieve this condition minimum cleaning time to remove the alginate layer has to be identified. It has been found that Fenton-like reactions take 10 min to complete [72], [73]. However, in this 10-minute, larger degradation of organic only happens during the first few minutes and as it approaches the end of reaction time, organic degradation becomes insignificant.

1, 5 and 10 min of cleaning duration were investigated. The permeability curve of this experiment are displayed by Figure B4 in Appendix B. The 5 and 10 minutes cleaning duration produced almost identical permeability profile, while 1 minutes cleaning gives insignificant fouling removal performance. Similar curves for 5 and 10 minutes filtration implies there is not much further degradation took place after 5 minutes reaction times.

4.2.5. Effect of cleaning interval

Although most of the cleaning can be done at any point in the filtration process, the effectiveness of the cleaning could be different, especially in the filtration of alginate. Change in the fouling layer properties or altered interaction of the chemicals involved during the cleaning reaction could

lead to the stronger fouling layer. To know what is the most optimum cleaning time, 40, 60 and 90 min of cleaning interval were tested.

As displayed in the Figure B5 in Appendix B the results indicate that 40 min cleaning interval always achieved a higher permeability recovery. The worst results were achieved at 90 min cleaning interval, where during the first cleaning, only 23% of permeability recovery was achieved. The results of this experiments confirm the theory raised by van den Brink [65] and Katsoufidou [31] who state that in the long run of high pressure filtration, alginate can be compacted and becomes irreversible.

4.2.5. Iron coating and forward flush

It can be seen from all the previous graphs that there was a declining pattern from the first to the second cleaning based on Fenton-like reactions. Based on the observations, between 50 to 80% reduction applied to all experiments. This could occur due to several reasons.

First, when cleaning was done some loosened layer and debris could still be weakly attached on the top of the alginate layer. As another alginate filtration starts and pressure builds up, this loosened layer can easily return back to its original form before any cleaning is applied, leading to the insignificant effect of Fenton-like reaction.

Second, the first cleaning by Fenton-Like reactions cannot remove the whole fouling layer, since none of the cleaning were able to reach 100% recovery, leaving some parts of the membrane surface covered by the fouling layer. As a result, once the second coating is applied, some of the iron will be attached to the fouling layer rather than on the membrane surface. As the filtration goes on, the existing layer of the alginate can be compacted and attract new alginate to stick on it, which makes the fouling even harder to remove.

This finding is leaving some space for improvement to remove the alginate layer thoroughly. One possible approach is by using forward flush at the end of every cleaning cycle to amplify the cleaning effect. Therefore, the experiments to investigate the cleaning interval and cleaning duration were repeated, and orward flush was applied after each cleaning with hydrogen peroxide. Permeability recoveries for conditions with and without forward flush are summarized in the Table 4.2.

Table 4.2. Permeability recovery before and after forward flush was applied

	Without Forward Flush			With Forward Flush		
	Experiment	Recovery (%)		Experiment	Recovery (%)	
		1st Cleaning	2nd Cleaning		1st Cleaning	2nd Cleaning
Cleaning Interval	40 min	69	23	40 min	72	50
	60 min	58	13	60 min	57	30
	90 min	13	2	90 min	35	8
	Experiment	Recovery (%)		Experiment	Recovery (%)	
		1st Cleaning	2nd Cleaning		1st Cleaning	2nd Cleaning
Cleaning Duration	1 min	14	8	1 min	36	15
	5 min	50	23	5 min	58	50
	10 min	69	23	10 min	58	51

Similar recovery for all the 1st cleanings, except for the 90 min cleaning interval and 1 min cleaning duration, show that forward flush was not needed in a condition where the Fenton-like reactions can proceed completely. If there is a debris that can return back on the membrane surface once forward flush is applied, the new results should have given a bigger permeability recovery since the initial permeability of the second filtration would then be higher. Increase in the recovery of the 1 min cleaning duration and 90 min cleaning interval, indicates that here the forward flush could help to increase fouling removal of incomplete Fenton-like reactions in the compacted gel layer.

The role of forward flush got more important in the second cleaning, where it doubled the recovery at all the cleaning durations and intervals in comparison to when forward flush was absent. Cleaning duration and filtration interval that was enough to remove the alginate layer during the first cleaning was insufficient, probably due to compaction of the alginate layer as the filtration process continued.

4.3. Iron oxide coating

Magnetite (Fe_3O_4) was also used as a source of the iron in the coating experiment. Magnetite structure contains both iron (II) and iron (III) ions which might lead to a greater extent of fouling removal since both Fenton and the Fenton-like reaction occurs at the same cleaning process. Validation of Fenton reaction and the effect of higher dosing concentration is reported in section 4.3.1.

4.3.1. Iron oxide Fenton reaction vs. blank experiment

This comparison aims to confirm if the iron oxide coating results in Fenton reactions, and to compare the fouling enhancement of the iron oxide coating to the iron hydroxide. Thus, blank solutions and Fenton experiments were compared. There were 4 different blank experiment tested: iron oxide coating without cleaning, iron hydroxide coating without cleaning, hydrogen peroxide cleaning without coating, and fouling experiment without any treatment. In the experiment where both iron oxides and hydrogen peroxide were present, the dosing coating solution was set to 400 mg/l. Permeability profile of each blank test and iron hydroxide can be seen in Figure 4.3.

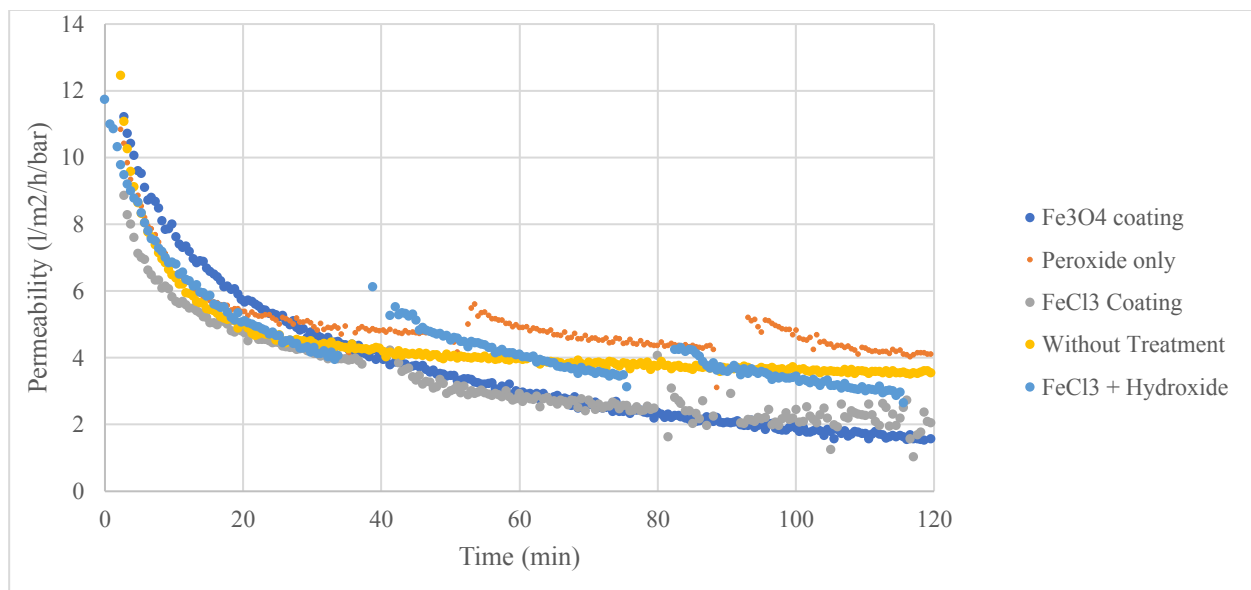


Figure 4.3. Results of blank test and 400 mg/l iron oxide Fenton reaction

According to Figure 4.3, the iron oxide coating gave an additional fouling attachment like in the iron hydroxide coating. The dark blue and grey dots represent a lower end permeability than the yellow line, which represents membrane filtration without any treatment. Figure 4.3 also shows that iron chloride reactions with hydrogen peroxide cleaning were less effective than a condition where only hydrogen peroxide was present, which might indicate that the Fenton reaction were insignificant for 400 mg/l coating.

Next, a higher concentration of the iron oxides dosing solution was tested to promote more Fenton reactions. 2440 mg/l iron oxide solution was injected into the system. However, both concentrations produced identical permeability curves which shows the poor performance of the magnetite particles in promoting the Fenton reaction during the cleaning process. The complete permeability curves of 2440 mg/l and 400 mg/l can be found in Figure C2 of Appendix C.

50-100 nm magnetite has a specific surface area of 60 m²/g [74]. However, compared to the amorphous structure of iron hydroxide flocs, the available surface area of magnetite is much lower. Amorphous iron hydroxide flocs can have a surface area of 316 m²/g [75], and this value can go

higher depends on the convexity of the floc itself [56]. This smaller surface area provided by iron oxide could be one of the factors that lead to less Fenton reaction.

4.4. Calcium carbonate coating

The first set of the calcium carbonate experiment were to have an indication of the effect of the reaction between calcium carbonate and acid. Later, other investigations on the types of acid used, dosing, and cleaning duration were also researched and represented in subsection 4.4.1 to 4.4.4. The feed pH was kept constant throughout all experiments at a value of 10 followed by 1 h of 40% amplitude sonication, to ensure best dispersion of calcium carbonate as colloid solution [57],[76]. Also, after each cleaning with acid solution forward flush was applied to maximize the foulant removal.

4.4.1. Calcium carbonate-acid reaction vs. blank experiment

Three different blank experiments were tested which were calcium carbonate coating without cleaning, citric acid cleaning without coating, and a pure fouling test without any treatment. The complete results can be seen in Figure D1 of Appendix D. The results show that the permeability curve of the calcium carbonate experiment (blue dots) was slightly higher than the pure fouling curve (yellow dots), which indicates that fouling enhancement did not occur. Furthermore, the experiment of 400 mg/l calcium carbonate coating with citric acid produced a better permeability curve than when only citric acid was present, confirming the significance of the reaction between the calcium carbonate and citric acid

4.4.2. Citric acid vs. Hydrochloric acid

Various acids can be used to promote a reaction with calcium carbonate to produce carbon dioxide, salt and water. Application in pollutant removal has shown that calcium carbonate can react with nitric acid and sulfuric acid [53],[77]. Formic acid has also been used in reaction with calcium carbonates in numerous researches [58],[78]. However, which acid can give the best reaction with calcium carbonate layer is not clear. A strong acid, such as hydrochloric acid with a low pH, might drive the reaction faster. Also, a polyprotic acid such as citric acid which has three acid functional groups in one molecule, and widely applied as a chelating agent, could also give a distinct interaction.

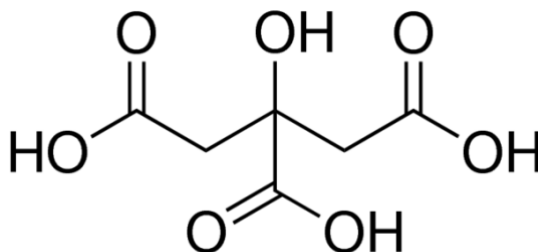


Figure 4.4. Citric acid structure [79]

Therefore, experiments with hydrochloric acid and citric acid to investigate the influence on fouling removal were conducted. Based on the cleaning experiments with hydrochloric acid and citric acid, as shown in Figure D2 of Appendix D, it can be concluded that citric acid performed better in recovering the permeability of the ceramic nanofiltration membrane. Every cleaning with citric acid showed a higher permeability than cleaning with a hydrochloric acid solution. Cleaning with hydrochloric acid did not give an improvement in recovering the permeability and gave a pattern as if there was no cleaning applied in between 120 min of sodium alginate filtration.

4.4.3. Effect of calcium carbonate dosing concentration

Different calcium carbonate concentrations with 40 minutes cleaning interval were also tested to know what is the minimum coating concentration that gives sufficient permeability recovery. 100 mg/l, 200 mg/l, and 400 mg/l of dosing were examined, and the complete permeability curves can be found in Figure D3 in Appendix D. 200 and 400 mg/l gives similar recovery that is higher than 100 mg/l, indicating that 100 mg/l coating was not enough for sufficient fouling removal. Thus, it can also be concluded that, here, 200 mg/l was the minimum dosing to promote the reaction between citric acid and calcium carbonate.

4.4.4. Effect of cleaning duration

Three different cleaning durations as shown in Figure 4.5 were investigated to find the minimum down time for the cleaning process. 1, 5 and 15 min of cleaning were applied to the experiment where cleaning was conducted after 40 min of filtration. All the three different cleaning durations produced similar permeability patterns, showing that 1 min was enough for the removal of the alginate fouling layer. In fact, it also indicates that calcium carbonate reactions with citric acid resulted in shorter cleaning times, compared to the ones given by iron hydroxide.

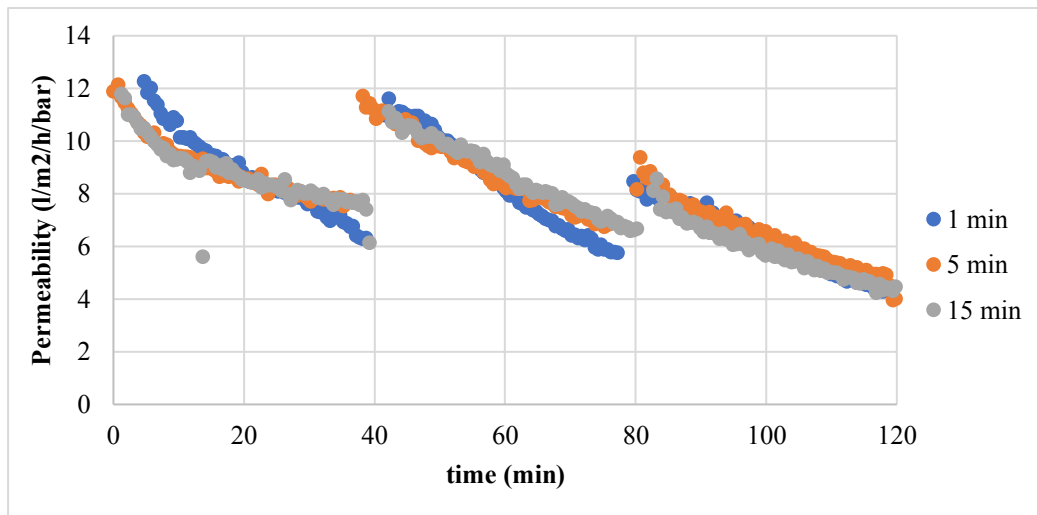


Figure 4.5. Permeability curve of 400 mg/l calcium carbonate coating in 3 different cleaning duration

4.5. Best case comparison of iron hydroxide and calcium carbonate

Both the iron hydroxide and the calcium carbonate coating seemed to give a considerable impact on retaining the membrane permeability high before chemical cleaning with 0.1 % NaOCl is needed. However, it was not clear the increase in average flux compared to the conventional practice where cleaning will only be done at the end of 2 h filtration process by 0.1 % sodium hypochlorite. In this chapter water productivity from the best condition of iron hydroxide and calcium carbonate dosing were compared to the condition where there was no treatment in the middle of 2 hours filtration, their permeability curve is depicted in Figure 4.6.

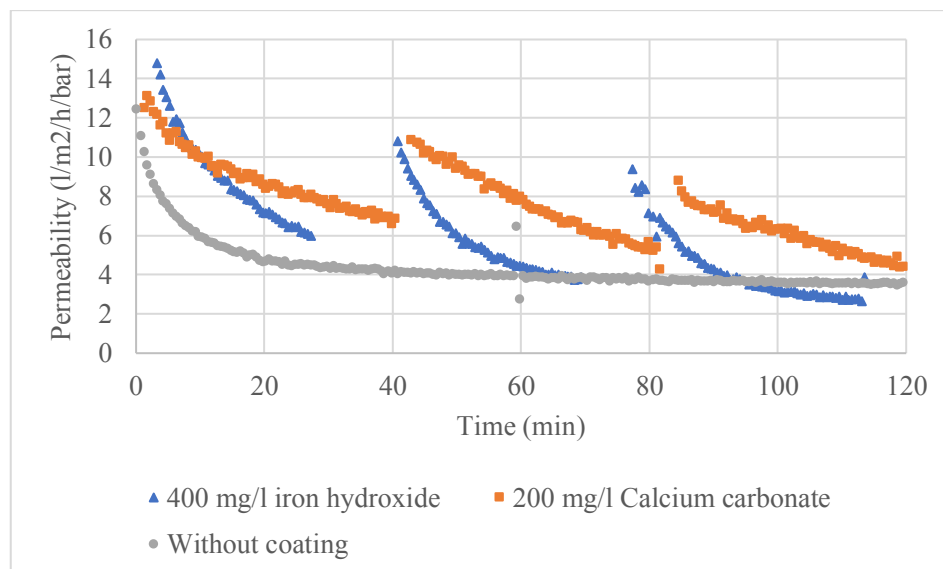


Figure 4.6. Permeability curve of the best condition for iron hydroxide and calcium carbonate coating compared to the condition when coating is absence

For iron hydroxide coating, 400 mg/l of dosing was used with 5 min of cleaning using a 400 mg/l hydrogen peroxide solution. Experiments with calcium carbonate were done with 1 min of cleaning with a 200 mg/l citric acid solution and a calcium carbonate dosing of 200 mg/l. In all of the

experiments, every 40 min alginate filtration was stopped and followed by a cleaning. In case of the coating with calcium carbonate and iron hydroxide, in the end of every cleaning 5 min forward flush was performed to enhance the removal of the fouling layer. In the condition where coating is absence there is nothing done before the chemical cleaning. In the end of all experiments chemical cleaning took place for 1 h to achieve perfect fouling removal. All the experiments were performed within 2 h of filtration, and all the average flux are shown in the Figure 4.7.

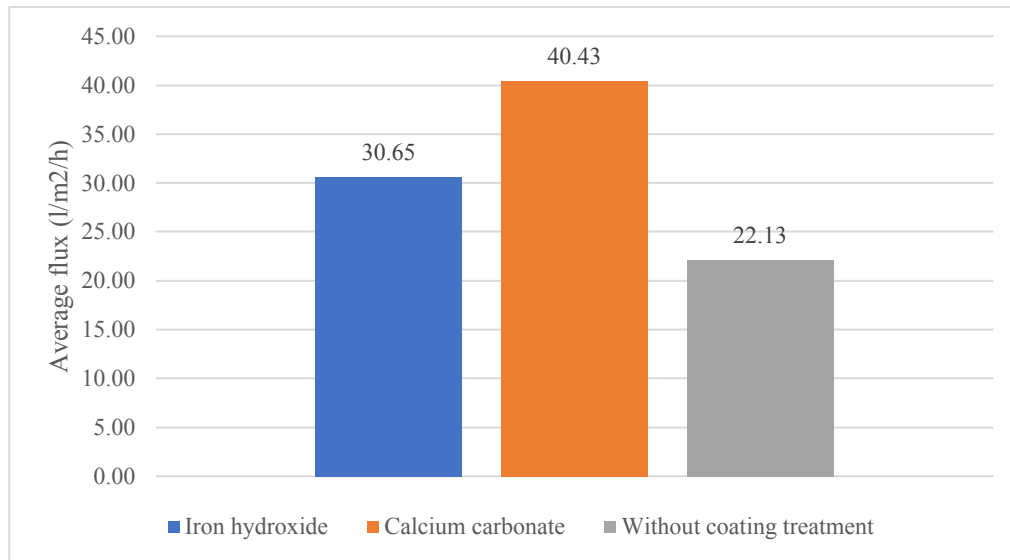


Figure 4.7. Water productivity of iron hydroxide, calcium carbonate coating, and chemical cleaning

Based on the Figure 4.7 both iron hydroxide and calcium carbonate coating had a higher average flux than condition where coating was absence. However calcium carbonate coating had a higher average flux, with 40.43 l/m²/h, compared to the iron hydroxide coating, with 30.65 l/m²/h flux. Although calcium carbonate coating has a higher flux, the economic and environmental study of the coating with calcium carbonate and iron hydroxide still needs to be done in order to get a comprehensive comparison between the various methods, which will be discussed in the next chapter.

5 Implementation of membrane coating in practice

5.1. Theoretical projection of coating process in the real sewage water

Further comparison of the calcium carbonate and iron hydroxide coating would require a projection of this method on a larger scale of filtration. This projection can bring a clearer image about economic and environmental burden if the coating method is implemented in the real filtration of sewage water. Limited research on the real scale application of C-NF membrane in treating sewage water, results in limited operational data available. The only closest real scale application to the ceramic membrane used in the lab scale experiment was done by Kramer [4], which was used in the calculation as a source of missing operational data for the practical application. It was assumed that once the precoating method is applied to filter the real sewage water, it will take 120 h as mentioned in the paper [4], to foul the membrane since it contained less alginate compare to synthetic sewage water. Furthermore, 1 m² C-NF membrane was used for every cleaning approach.

The upscaling and economic calculation of ceramic nanofiltration coating was done by following several steps mentioned below:

- Identification of important parameters
- Upscaling factor calculation
- Theoretical calculation of the coating process in real sewage water filtration
- Economical calculation of iron and calcium carbonate coating

Aforementioned steps will be explained in the next subchapters.

5.1.1. Identification of important design parameter

At this stage several data collected from the experiments, such as the required amount of iron and calcium carbonate deposited on the membrane surface to protect against fouling, duration of cleaning for each cleaning methods, and duration of forward flush are listed in the Table 5.1 and 5.2. Furthermore, water flux in the theoretical projection was taken from the average flux data as shown in subchapter 4.5.

Table 5.1. Design basis parameter for upscaling calculation for iron hydroxide coating

<i>Coating Data</i>	<i>unit</i>	<i>value</i>	<i>Source</i>	<i>Notes</i>
iron deposited on membrane surface	mg	210	experimental result	For 1 set of filtration cycle
iron chloride coating duration	minutes	20	experimental setup	two coating per filtration cycle
Hydrogen peroxide cleaning duration	minutes	10	experimental setup	two cleaning per filtration cycle
Forward flush cleaning duration	minutes	10	experimental setup	two cleaning per filtration cycle
Sodium hypochlorite cleaning	hours	1	experimental setup	1 chemical cleaning per filtration cycle
Hydrogen peroxide concentration	mg/l	400	experimental setup	
Sodium hypochlorite concentration	%	0.10	experimental setup	
Water flux in larger membrane	l/m ² /h	30	Projection from experiment results	Water productivity of small membrane/area of small membrane

Table 5.2. Design basis parameter for upscaling calculation for calcium carbonate coating

<i>Coating Data</i>	<i>unit</i>	<i>value</i>	<i>Source</i>	<i>Notes</i>
calcium carbonate deposited on membrane surface	mg	190	experimental result	For 1 set of filtration cycle
calcium carbonate coating duration	minutes	20	experimental setup	two coating per experiment
citric acid cleaning duration	minutes	2	experimental setup	two cleaning per experiment
Forward flush cleaning duration	minutes	10	experimental setup	two coating per experiment
Sodium hypochlorite cleaning	hours	1	experimental setup	1 chemical cleaning per experiment
citric acid concentration	mg/l	200	experimental setup	
Sodium hypochlorite concentration	%	0.10	experimental setup	
Water flux in larger membrane	l/m ² /h	40	Projection from experiment results	Water productivity of small membrane/area of small membrane

5.1.2. Upscaling factor calculation

Upscaling factor was calculated based on the 1 m² large membrane surface area used in the real sewage water filtration divided by surface area of the membrane used in the laboratory. The value of each surface area and the calculated extrapolation factor are shown in the Table E 6 of Appendix E. The linearization factor as calculated, was 614.

5.1.3. Theoretical calculation of coating process in the real sewage water filtration

In making the calculation of the projection from the lab scale results to full scale sewage water filtration, the following assumptions were taken:

- The whole filtration process for precoat method will also last for 120 h as done by Kramer et al [4].
- The whole operation for precoat method consisted of: 2 precoat process, 3 filtration and 2 cleaning (as in the experiment).
- The amount of deposited iron and calcium was extrapolated based on the upscaling factor.
- Same cleaning duration as in the experiment applied to the upscaling calculation.
- Cleaning solution (hydrogen peroxide and citric acid) required by the system was twice the void volume of the membrane.
- For the forward flush, it was assumed that feed sewage water will be used to clean up the membrane.

Complete calculation and the data used for both calcium carbonate and iron hydroxide system can be seen in the Appendix E and F for iron and calcium carbonate coating respectively.

Based on the data from experimental results, real sewage water filtration with ceramic NF and several assumptions mentioned above, calculation results as shown in Table 5.3 and 5.4 for iron hydroxide and calcium carbonate coating are obtained.

Table 5.3. Upscaled calculation result for iron hydroxide coating

Components	Units	Value	Specification
Effective filtration time per year	hours/year	8626	
Produced water	m ³ /year	268	
Required iron chloride for coating	kg/year	9.42	
Required peroxide solution	m ³ /year	0.032	400 mg/l concentration
	kg/year	0.013	pure peroxide
Required hypochlorite	kg/year	0.032	0.1 % solution

Table 5.4. Upscaled calculation result for calcium carbonate coating

Components	Units	Value	Specification
Effective filtration time per year	hours/year	8648	
Produced water	m ³ /year	352	
Required calcium carbonate for coating	kg/year	8.48	
Required citric acid solution	m ³ /year	0.032	200 mg/l concentration
	kg/year	0.007	pure citric acid
Require hypochlorite solution	kg/year	0.032	0.1 % solution

Based on Table 5.3 and 5.4 it can be seen that coating with calcium carbonate resulted in higher water production due to the higher water productivity as shown in Figure 4.7. Furthermore, faster reaction times of calcium carbonate with citric acid also gives more time available for the filtration process. In addition, calcium carbonate coating also has a lower resource consumption due to the lower amount of calcium carbonate needed to react with citric acid compared to the amount of iron hydroxide needed to trigger the Fenton-like reaction.

5.1.4. Cost estimate

Next, after calculating the required resources and total water produced in 1 year for calcium carbonate and iron hydroxide, the coating cost of each process was calculated. The cost component was divided into two parts, which are capital expenditures and operational expenditures. Capital expenditure refers to the money spent by the company to acquire a fixed asset such as land, building and also equipment. On the other hand, operational expenditures are variable costs.

In case of the capital expenditure, both calcium carbonate and iron hydroxide coating have similar value since the biggest component in capital investment is 1 m² ceramic nanofiltration membrane that is identical for every methods. However, in terms of the operational expenditure, there is a sharp difference between the methods. The operational expenditure for calcium carbonate is 0.12 euro/m³ water produced while water production with iron hydroxide coating required 0.22 euro/m³ water produced. These two values is still lower compare to the operational cost of only cleaning with 0.1 % sodium hypochlorite after 2 h filtration, 0.33 euro/m³ water produced. Lower operational cost of calcium carbonate coating is caused by the lower cost, less consumption of calcium carbonate and higher average flux than the iron hydroxide coating. The details of each iron hydroxide and calcium carbonate cost component can be seen in Appendix H.

5.2. Life cycle analysis

To assess the potential environmental impact caused by the iron hydroxide and calcium carbonate coating, Life Cycle Assessment (LCA) investigation was conducted. LCA is a tool that is widely used to assess the environmental effect of technology and product [80]. LCA examined every

material and utility input required to get a particular product so that the analyst can use the result to determine how environmentally friendly a product is. A comprehensive LCA assess every stage that involves in delivering a product such as extraction of raw materials, pretreatment, production process, product distribution and the disposal [81].

According to Thannimalay [82] LCA consists of several steps:

- Project definition: a stage where the objective and the scope of the LCA is defined
- Model preparation: details of the production process are assessed, including all the inflow and outflow of the process. Sometimes, this stage is also recognized as a life cycle inventory
- Impact assessment: Every component of the stream are categorized at a specific area where it affects the environment.
- Interpretation of the result

In the following sub-subchapter iron hydroxide and calcium carbonate coating will be assessed based on the steps mentioned above.

5.2.1. Project definition

The goal of the project is to evaluate and compared the environmental impact caused by two different coating methods which are iron hydroxide and calcium carbonate to the 1 hour cleaning of sodium hypochlorite, In order to remove the membrane fouling during water filtration using ceramic nanofiltration membrane. To do so, the functional unit of the membrane coating process need to be defined. The functional unit serves as a base in which the technology will be compared [83], most of the time it is the unit of product which in this case is 1 m³ of the clean water produced.

5.2.2. Model preparation

In the model preparation, a simple box flow diagram that illustrates water production of filtration using ceramic nanofiltration is created. This diagram helps to identify what are the input and output component such as energy, raw materials, and products. Figure 5.1, Figure 5.2 and Figure 5.3 show box flow diagram of calcium carbonate coating, iron hydroxide and cleaning with 0.1 % NaOCl after 120 h of filtration.

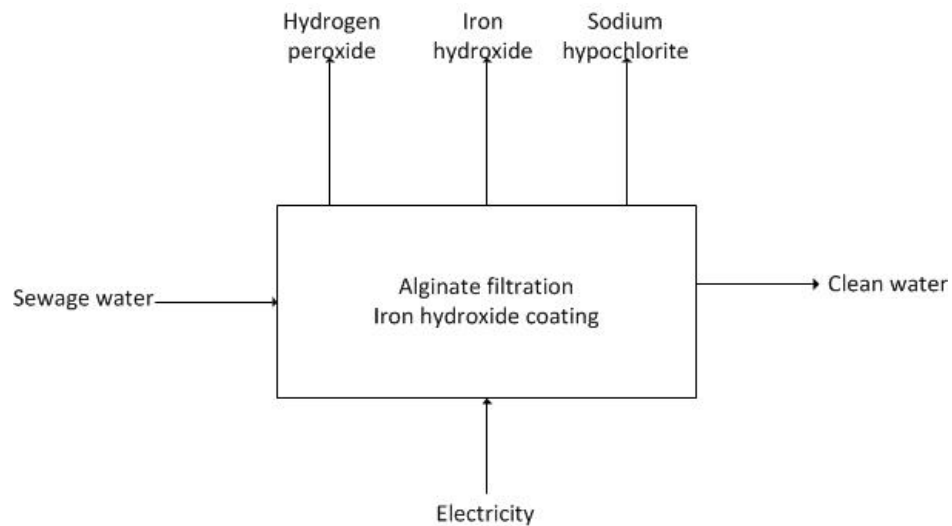


Figure 5.1. Block flow diagram for alginate filtration using iron hydroxide

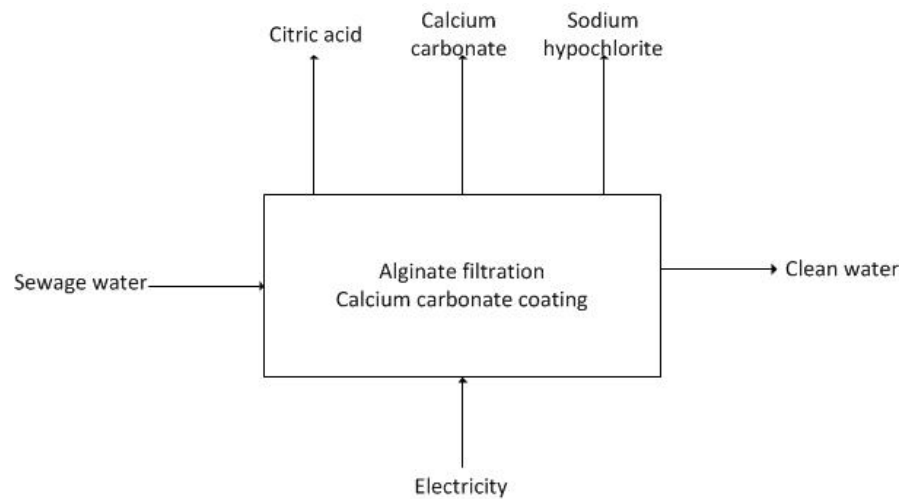


Figure 5.2. Block flow diagram for alginate filtration using calcium carbonate coating

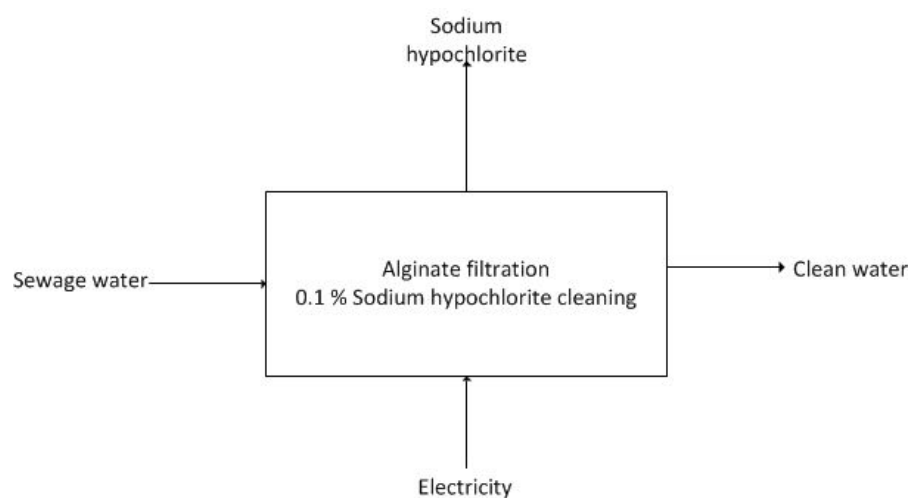


Figure 5.3. Block flow diagram for alginate filtration with 0.1 % sodium hypochlorite cleaning

Further, the size of all identified streams that are required or wasted to produce 1 m³ of clean water, using both iron hydroxide and calcium carbonate are listed in the Table I1 and Table I6 of Appendix I. The data for citric acid, calcium carbonate, and sodium hypochlorite were obtained from the upscaling calculation as mentioned in subchapter 5.1, Appendix E and, Appendix F but instead of using total yearly production, 1 m³ of clean water was used as a basis. Therefore, all values in the Table 5.3 and 5.4 were divided by yearly clean water production in each process. The same upscaling calculation was also conducted for conventional cleaning which can be found in Appendix G.

Fuel production and its waste gas were defined based on life cycle assessment produced by Cooper [84]. Method with higher membrane flux will have lower electricity consumption due to less resistance in production 1 m³ water. Complete fuel production, electricity production, disposal of citric acid and hydrogen peroxide data and its source can be found in Appendix I.

To simplify the iron and calcium carbonate coating life cycle assessments, the inventory and further categorization process were supported by the CMLCA software, produced by Leiden University. Chemical components as mentioned in Table 5.3, Table 5.4 and in Table G8 of Appendix G for sodium hypochlorite are defined in the software by creating a new process called sodium alginate filtration. The complete results of total inventory calculations, including fuel production process, were as follow:

Table 5.5. Inventory calculation results by CMLCA program for Iron hydroxide coating

Component	Value	Unit
Sodium hypochlorite	1.2 x 10 ⁻⁴	m3
Iron (resources)	0.035	kg
Hydrogen peroxide	4.8 x 10 ⁻⁵	kg
Oil crude	0.084	kg
Carbon dioxide	0.1	kg
Sulphur dioxide	0.012	kg
Sewage water	-2	m3

Table 5.6. Inventory calculation results by CMLCA program for calcium carbonate coating

Component	Value	Unit
Sodium hypochlorite	9.1 x 10 ⁻⁵	kg
Calcium (resources)	0.024	kg
Citric acid	3.6 x 10 ⁻⁵	kg
Oil crude	0.049	kg
Carbon dioxide	0.058	kg
Sulphur dioxide	0.0068	kg
Sewage water	-2	m3

Table 5.7. Inventory calculation results by CMLCA program for cleaning with 0.1% of sodium hypochlorite after 120 h alginate filtration.

Component	Value	Unit
Sodium hypochlorite	2.48×10^{-4}	kg
Oil crude	-0.16	kg
Carbon dioxide	0.192	kg
Sulphur dioxide	0.0224	kg
Sewage water	-2	m ³

5.2.3. Impact assessment

In impact assessment, all the listed input and output flow for water production are categorized based on their potential destruction on a specific area of the environment. This categorization also involved the conversion of this component into a common unit of impact [85]. There are several categories in which environmental impact can be grouped, a method such as CML 2002, IMPACT 2002+, LUCAS, ReCiPe, and EPS 2002 are among the methods that widely to categorized environmental impact. Each of these methods has a specific unit that differs from one to another.

In this study, Eco-indicator 99 (EI-99) was chosen as a categorization method. The final product of Eco-indicator 99 is a single value output which allows the product or process designer to compare and decide which product has the least environmental burden [86]. Impacts are categorized into three different damages which are damage to human health, ecosystem quality, and resources. These categories will further be divided into several midpoints category as displayed in Table 5.8.

Table 5.8. Damage and midpoint category for Eco-indicator 99 [87]

Damage category	Midpoint impact category
Damage to human health	Carcinogenic effects
	Respiratory effects (inorganic)
	Respiratory effects (organic)
	Climate change
	Radiation
	Ozone depletion
Damage to ecosystem quality	Ecotoxicity
	Acidification / eutrophication
	Land use
Damage to Resources	Minerals
	Fossil

Based on the input processes defined in CMLCA software, the contribution of each chemical to the damage in Table 5.8 was calculated from baseline values for characterization, also produced by Leiden University [88]. This value was obtained from Handbook on LCA such as GWP100, POCP, HTPinf and AP [89]. The results of this categorization are as follow:

Table 5.9. Eco-indicator categorization result for iron hydroxide using the Eco-indicator 99 method calculated with CMLCA

Component	Value	Units
Respiratory effects on human caused by inorganic substances	6.4×10^{-7}	DALY
Carcinogenic effects on human	1.6×10^{-9}	DALY
Damages to human health caused by climate change	2.1×10^{-8}	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	1.2×10^{-2}	PDF*m2*yr
Damages to resources caused by mineral extraction	1.8×10^{-3}	MJ
Damages to resources caused by fossil fuel extraction	0.51	MJ

Table 5.10. Eco-indicator categorization result for calcium carbonate using Eco-indicator 99 method calculated with CMLCA

Categorization	Value	Units
Carcinogenic effects on human	1.2×10^{-9}	DALY
Respiratory effect caused by inorganic substances	3.7×10^{-7}	DALY
Damages to human health caused by climate change	1.2×10^{-8}	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	7.1×10^{-3}	PDF*m2*yr
Damages to resources caused by fossil fuel extraction	0.29	MJ

Table 5.11. Eco-indicator categorization result for 0.1 % NaOCl using Eco-indicator 99 method calculated with CMLCA

Categorization	Value	Units
Carcinogenic Effect on Humans	2.8×10^{-9}	DALY
Respiratory effect caused by inorganic substances	1.2×10^{-6}	DALY
Damages to human health caused by climate change	4.0×10^{-8}	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	2.3×10^{-2}	PDF*m2*yr
Damages to resources caused by fossil fuel extraction	0.97	MJ

5.2.4. Interpretation of the result

To compare the environmental impact of iron chloride and calcium carbonate coating, single value results from Eco-indicator 99 need to be produced. To do that, normalization and weighting need to be done based on the value displayed in Table 5.9 to Table 5.11. Normalization is a way of quantifying the magnitude of the impact to a reference condition [85]. The reference condition usually is the value of impact per capita, which is the measure of total impact produce to certain damage category regionally divided by total population [86], in Eco-indicator 99 this value refers to European condition.

Last, weighting is done for each category. Weighting decides how many portions of the single score belongs to specific damage category. This process was done by having a group discussion with a lot of panelists to decide the value [87]. In Eco-indicator there are three different weighting types available: egalitarian, individualist, and hierarchist [90]. By default, hierarchist weighting was chosen in the calculation, since it has balance long and short-term perspectives consideration. Human health and ecosystem damage are considered to be equally important while damage to a resource would have a half value of the other damage [91]. The complete weighting value can be seen in Appendix I. Table 5.12 shows single value results of both calcium carbonate and iron hydroxide coating.

Table 5.12. LCA single value score for iron hydroxide and calcium carbonate coating based on EI-99 indicator

	LCA Weighted Index
Iron hydroxide coating	3.02×10^{-5}
Calcium carbonate coating	1.75×10^{-5}
0.1 % sodium hypochlorite	5.76×10^{-5}

LCA weighted index in the Table 5.12 shows iron hydroxide coating has greater environmental burden compares to calcium carbonate. In both cases, the highest contributor to the weighted index value is carbon dioxide and sulfur dioxide that are produced from fuel and electricity production. Therefore, lower energy consumption of calcium carbonate results in lower LCA single value. Another contributor to the difference LCA single value comes from the greater resources depletion from the extraction of the iron component in the coating with iron hydroxide. However, both of the coating process produced lower total score compared to the 0.1 % sodium hypochlorite cleaning.

6 Conclusions and recommendations

6.1. Conclusions

In this subchapter the answer to the research questions as mentioned in the chapter 1 will be summarized:

1. *What is/are (a) potential physical cleaning method(s) that can be applied on a ceramic NF membrane?*
2. *How effective is the potential physical cleaning in removing a fouling layer from a ceramic NF membrane?*

Forward flush was tested in this research due to its potential ability to clean up the fouling layer without damaging the membrane surface. Investigation on the cross flow velocity, and cleaning duration show that once the minimum cross flow velocity (0.4 m/s) and cleaning duration (3 min) was achieved the permeability recovery did not change. Furthermore, shorter cleaning intervals resulted in less filtration time which reduced the water productivity, during 2 h of operation. Based on the experimental results, the application of forward flush did not give a sufficient fouling removal. However, in combination with other cleaning methods, such as calcium carbonate and iron hydroxide coating, forward flush was able to double the initial performance of both coating methods.

3. *What is/are (an) other potential technique(s) to protect or remove fouling from the membrane surface?*
4. *How effective is/are the new technique(s) to protect or remove fouling from membrane surface?*

Iron hydroxide – hydrogen peroxide, and calcium carbonate – citric acid, which followed by forward flush were able to achieve more than 60 % of permeability recovery. Iron hydroxide was able to promote Fenton reactions with 400 mg/l dosing and 400 mg/l hydrogen peroxide with minimum reaction times of 5 min. On the other hand, calcium carbonate only required 200 mg/l of dosing to trigger reactions with 200 mg/l citric acid with a minimum cleaning duration of 1 min. In the 2 h filtration experiment, filters with a calcium carbonate coating produced a higher water productivity than using an iron hydroxide coating. In the end, the water productivity of filters with both iron hydroxide and calcium carbonate was higher than conventional operation where cleaning with 0.1 % sodium hypochlorite for 1 h was done after the 2 hour filtration.

5. *How large are the costs and environmental impact of the successful methods during practical implementation for sewage water treatment?*

Environmental and economic impact of iron and calcium carbonate coatings for fouling control of ceramic membranes were assessed by projecting the experimental data to the application of ceramic NF as described by Kramer et al [4]. Cost of production per m³ of water was estimated to be 0.22 euro when using iron hydroxide coating and 0.12 euro in the case of calcium carbonate.

Furthermore, environmental impact assessment using CMLCA software with Eco-indicator 99 categorization showed that, all the coating methods produced lower total score than cleaning with 0.1 % sodium hypochlorite after 120 hour of sewage water filtration. However, the application of calcium carbonate coating was calculated to have an even lower environmental burden compared to the use of iron hydroxide.

6.2. Recommendations

This lab research has successfully demonstrated that iron and calcium carbonate coating with their cleaning solution are able to effectively remove a fouling layer formed by the sodium alginate. From this point, further research should be carried out to get better information on the full implementation of this method in real sewage water filtration. This information is described below.

6.2.1. Experimental Improvement

A more detailed study on the membrane coating process has to be carried out. In this study it might be necessary to break the membrane structure and to look for the phenomena that are happening on its surface. This kind of experiment is essential to get a better insight to optimize the coating process. The distribution of the materials on the top of the membrane surface is critical to minimize the required coating materials. Furthermore, it is also important to make sure that the membrane surface is covered for 100 % with the coating. If the research on coating materials has been carried out and indicates that the current methods did not achieve 100 % membrane coverage, an improvement that can result in full coverage of the membrane surface will increase the effectivity of Fenton-like reactions and calcium carbonate-acid dissolution.

6.2.2. Membrane coating in the real sewage water

In addition, the coating experiment of the larger membrane with the real sewage water should be done. By doing so, the data about the resources loss when upscaling from small membrane to a larger membrane can be obtained. Also, this research could provide a real value of lower water productivity due to the enhancement of fouling caused by iron coating layer which might be different to the value obtained from the experimental results of small C-NF membrane. This kind of experiment will yield to actual water productivity data for membrane coating which also results in more accurate LCA calculations. Furthermore, the environmental impact assessment could also be done with other LCA software such as Simapro to validate the current results with another database.

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Appendix A

Forward Flush Experiment Results

A1. Forward flush duration investigation

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Alginate filtration duration: 40 minutes
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution (0.8 g/l)
- Forward flush cross flow velocity: 1.1 m/s
- Pressure during forward flush: 0 bar

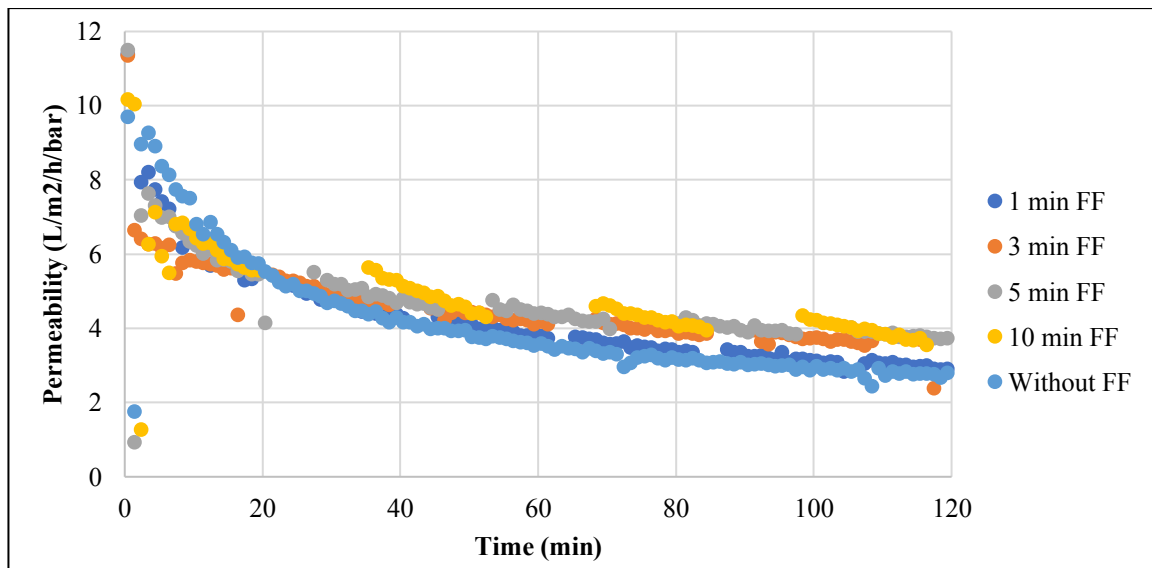


Figure A1. Forward flush duration investigation results

A2. Comparison of early 10 minutes cleaning interval flush vs constant 20 minutes cleaning interval

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution (0.8 g/l)
- Forward flush duration: 5 minutes
- Forward flush cross flow velocity: 1.1 m/s
- Pressure during forward flush: 0 bar

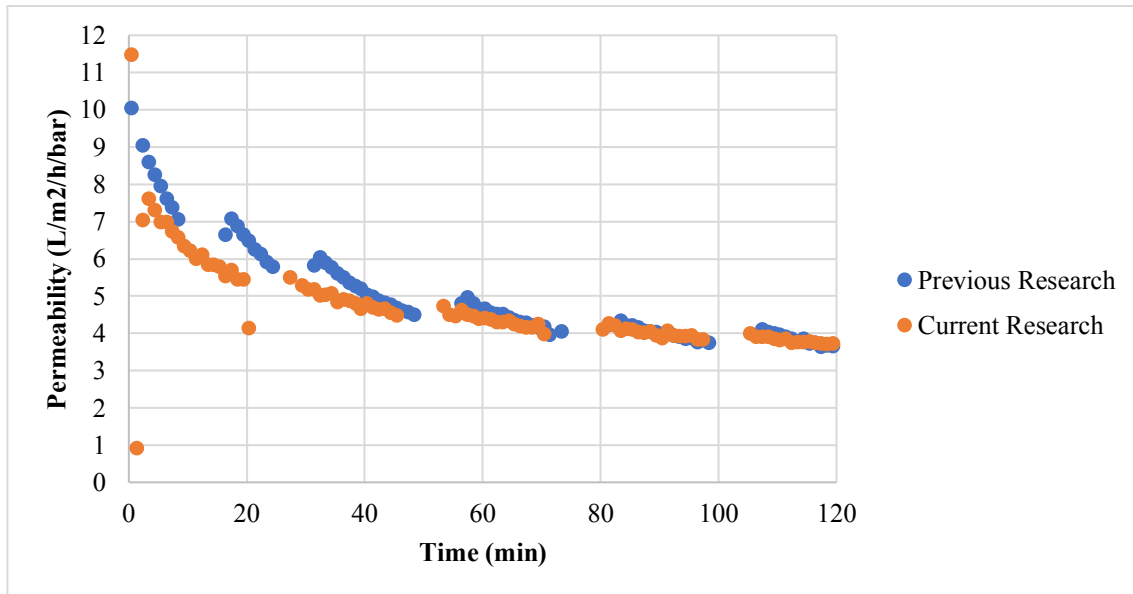


Figure A2. Early 10 minutes cleaning interval vs constant 20 minutes cleaning interval

A3. Cleaning interval investigation results

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Forward flush duration: 5 minutes
- Forward flush cross flow velocity: 1.1 m/s
- Pressure during forward flush: 0 bar

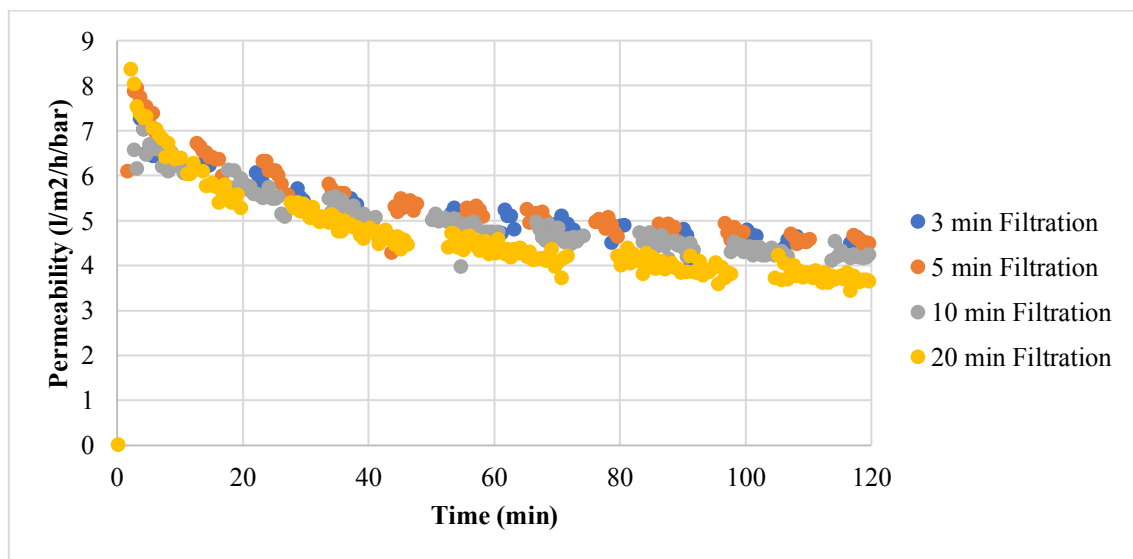


Figure A3. Cleaning interval investigation permeability curve results

Appendix B

Iron hydroxide coating experiment results

B1. Blank experiment result vs 400 mg/l iron hydroxide Fenton reaction

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l
- pH of feed coating solution: 7
- Cleaning duration: 10 minutes
- Cleaning pH: 2.5

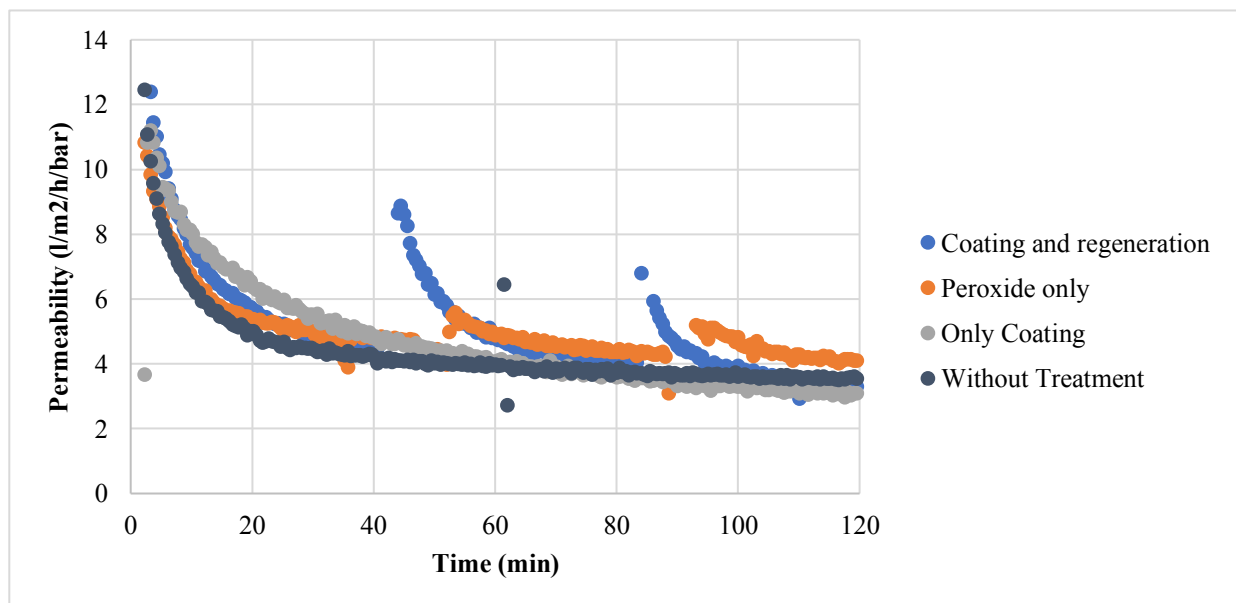


Figure B1. Permeability curve of blank experiment and 400 mg/l iron hydroxide Fenton reaction

B2. Dosing concentration investigation results

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l

- pH of feed coating solution: 7
- Cleaning duration: 10 minutes
- Cleaning pH: 2.5

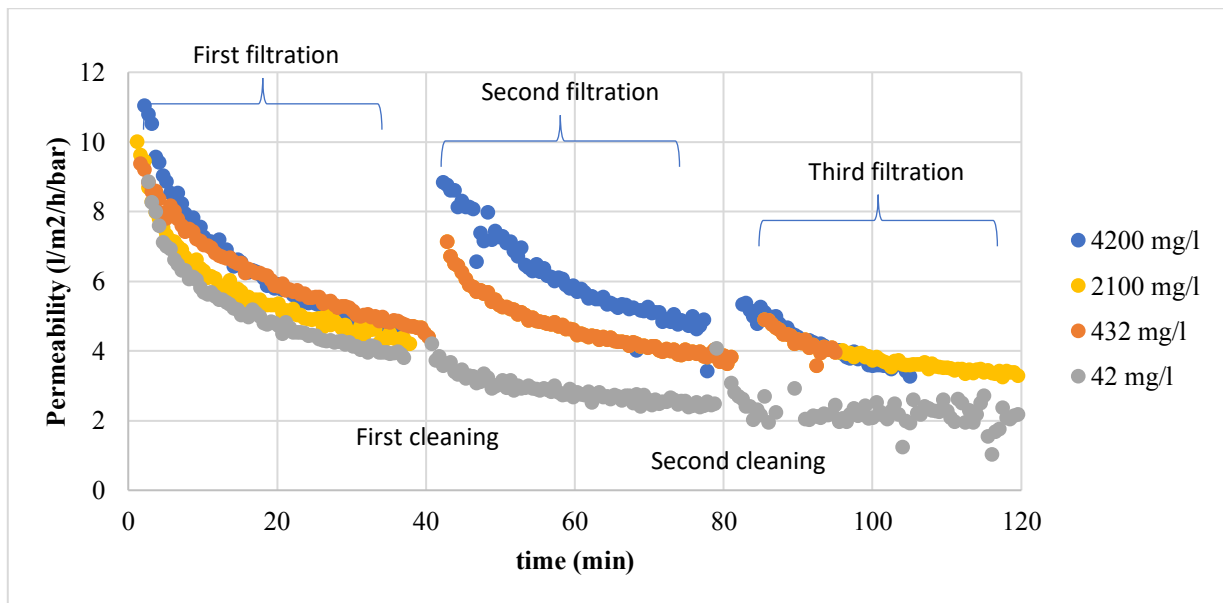


Figure B2. Permeability curve of several iron dosing concentration experiment

Table B1. Measured feed concentration and deposited amount of iron

	Iron Dosage Concentration (mg/l)							
	4200		2100		432		42	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	307	342	251	244	21	32	0.58	0.7
Iron (III) coated (mg)	493.8	328.4	484.2	759	91.7	102.2	0.2	0.2

B3. Feed pH investigation results

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l
- Cleaning duration: 10 minutes
- Cleaning pH: 2.5

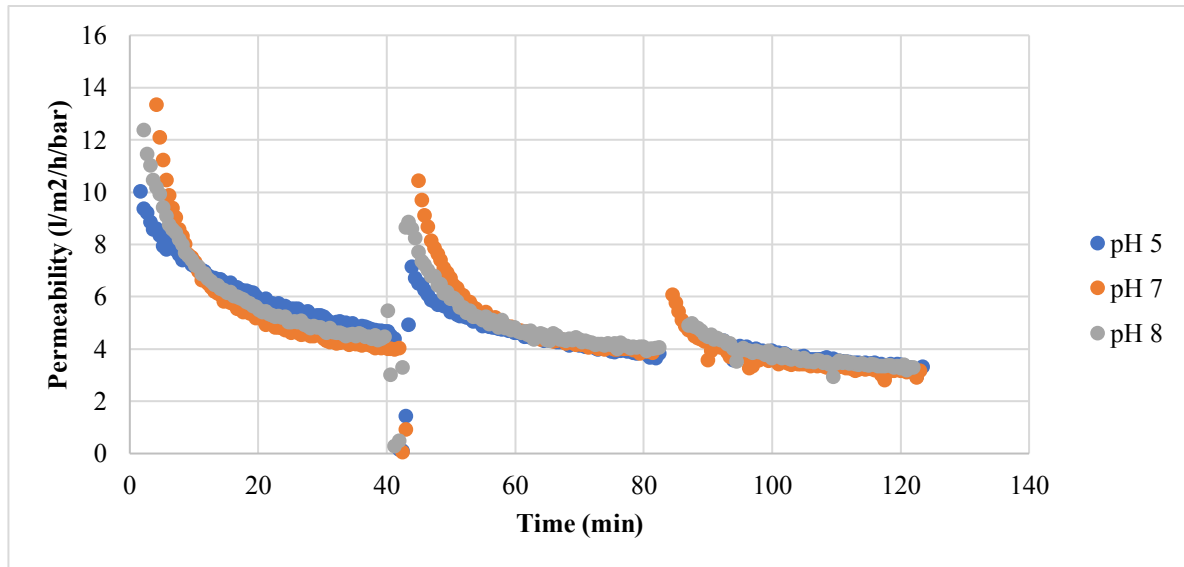


Figure B3. Permeability curve of pH investigation experiment

Table B2. Measure feed concentration and deposited iron during pH investigation experiment

	Feed pH					
	5		7		8	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	53	33	53	28	47	32
Iron (III) coated (mg)	400	226.7	125	166.7	100.54	100.25

Table B3. Permeability recovery results of pH investigation experiment

Recovery (%)	pH		
	5	7	8
First cleaning	48	69	53
Second cleaning	17	23	11

B4. Cleaning duration investigation results

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l
- Coating pH: 7
- Cleaning pH: 2.5

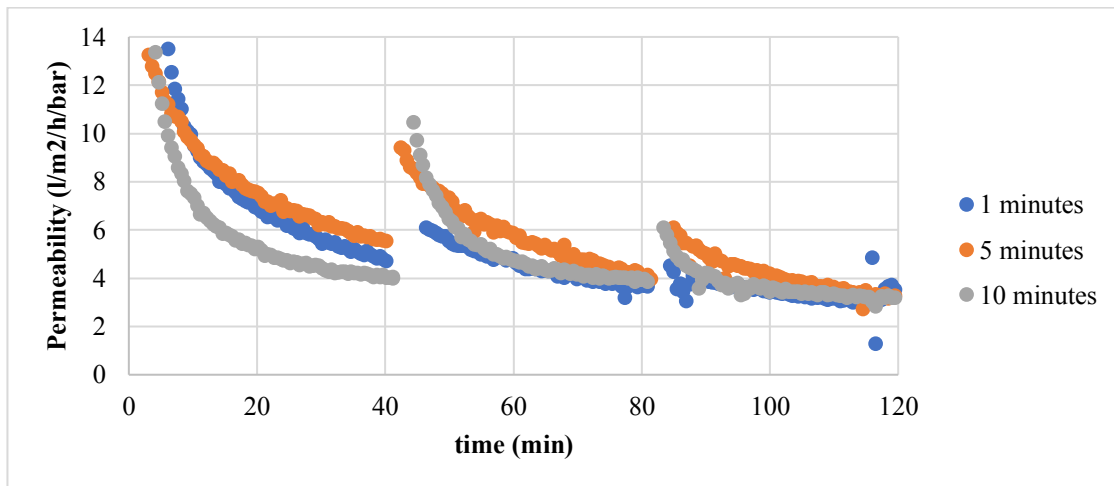


Figure B4. Permeability curve of pH investigation experiment

Table B4. Measure feed concentration and deposited iron during cleaning duration experiment

	Cleaning Duration (min)					
	1		5		10	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	74	97	46.3	30	53	28
Iron (III) coated (mg)	400.47	508.65	109.08	188.35	125.63	166.67

Table B5. Permeability recovery results of cleaning duration experiment

Experiment	Recovery	
	1st Cleaning	2nd Cleaning
1 min	14	8
5 min	50	23
10 min	69	23

B5. Cleaning interval investigation results

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning duration: 10 minutes
- Iron dosing concentration: 400 mg/l
- Coating pH: 7

- Cleaning pH: 2.5

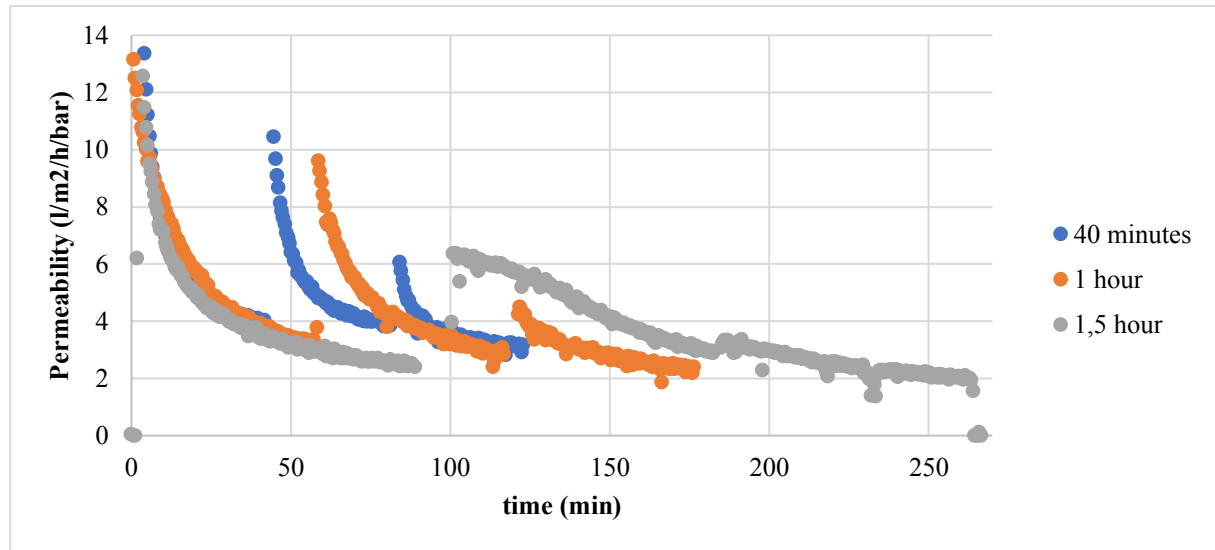


Figure B5. Permeability curve of cleaning interval experiment

Table B6. Measure feed concentration and deposited iron during cleaning interval experiment

	Cleaning Interval (min)					
	40		60		90	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	53	33	223	448	74	97
Iron (III) coated (mg)	125.67	226.7	1500	205	400	508

Table B7. Permeability recovery results of cleaning interval experiment

Experiment	Recovery	
	1st Cleaning	2nd Cleaning
40 min	69	23
60 min	58	13
90 min	13	2

B6. Cleaning duration investigation & forward flush

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning duration: 10 minutes
- Iron dosing concentration: 400 mg/l
- Coating pH: 7
- Cleaning pH: 2.5

- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

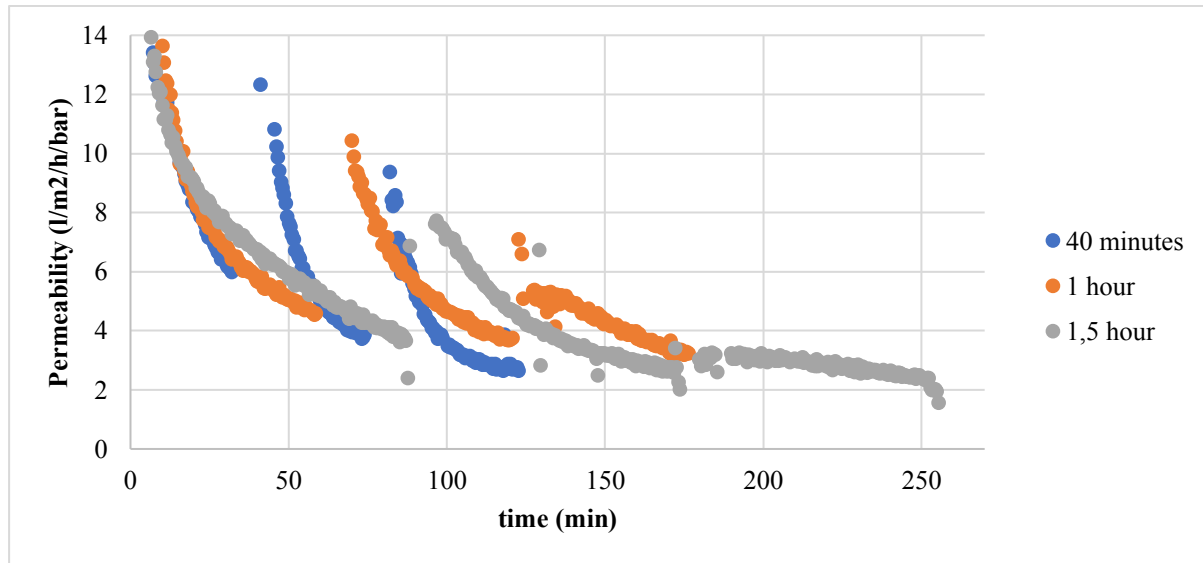


Figure B6. Permeability curve of cleaning duration and forward flush experiment

Table B8. Measure feed concentration and deposited iron during cleaning duration and forward flush experiment

	Cleaning Interval (min)					
	40		60		90	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	72	63	84	69	80	42
Iron (III) coated (mg)	151	59	318	100	168	92

B7. Cleaning duration & forward flush investigation

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l
- Coating pH: 7
- Cleaning pH: 2.5
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

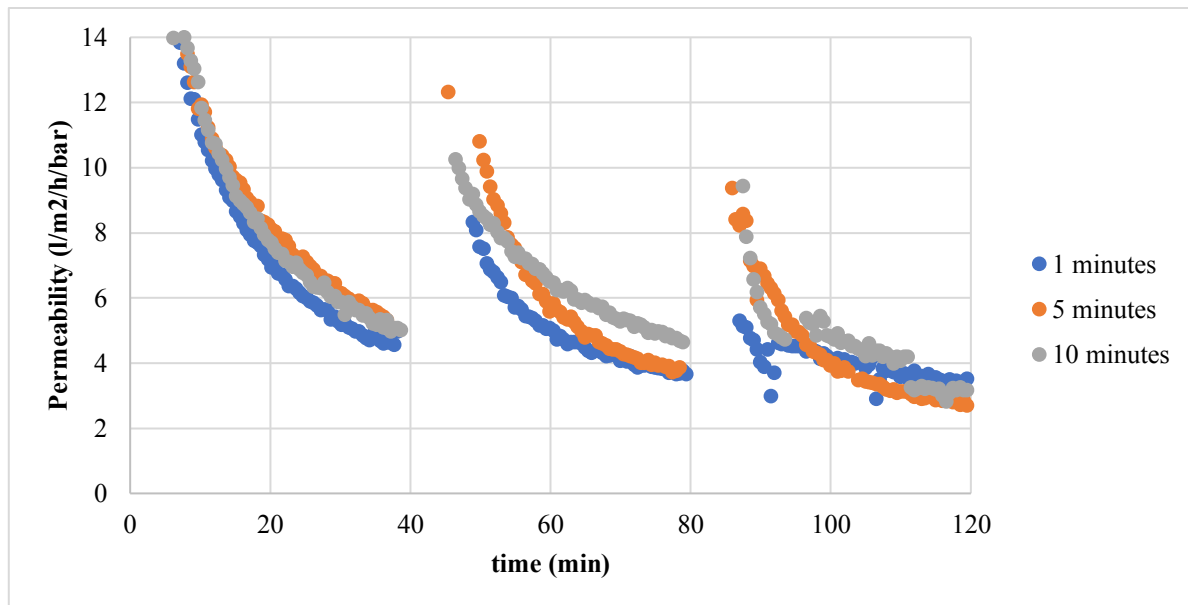


Figure B7. Permeability curve of cleaning duration and forward flush experiment

Table B9. Measure feed concentration and deposited iron during cleaning duration and forward flush experiment

	Cleaning Duration (min)					
	1		5		10	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Iron (III) feed concentration (mg/l)	64	55	223	73	72	73
Iron (III) coated (mg)	209	117	1509	225	109	225.

Appendix C

Iron oxide coating experiment results

C1. Blank experiment result vs 400 mg/l iron oxide Fenton reaction

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Iron dosing concentration: 400 mg/l
- Coating pH: 10
- Cleaning pH: 2.5
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

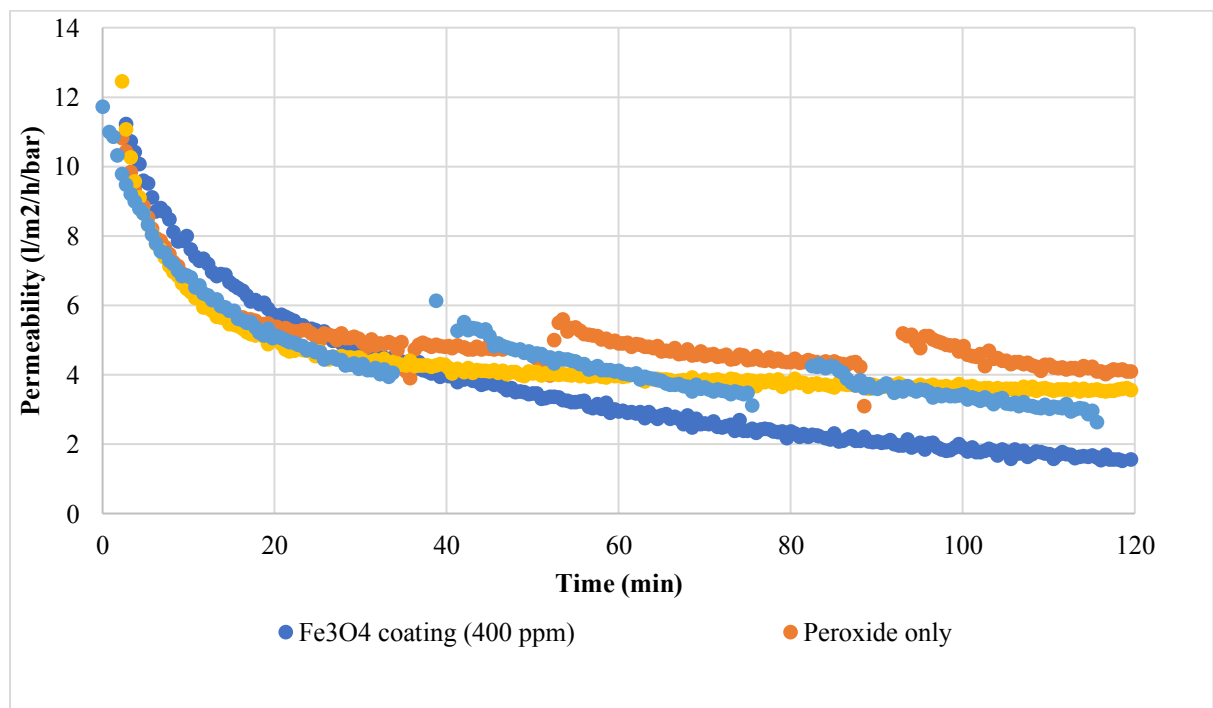


Figure C1. Permeability curve of blank experiment and 400 mg/l iron oxide Fenton reaction

C2. 2400 mg/l and 400 mg/l iron oxide Fenton reaction

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Coating pH: 10
- Cleaning pH: 2.5
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

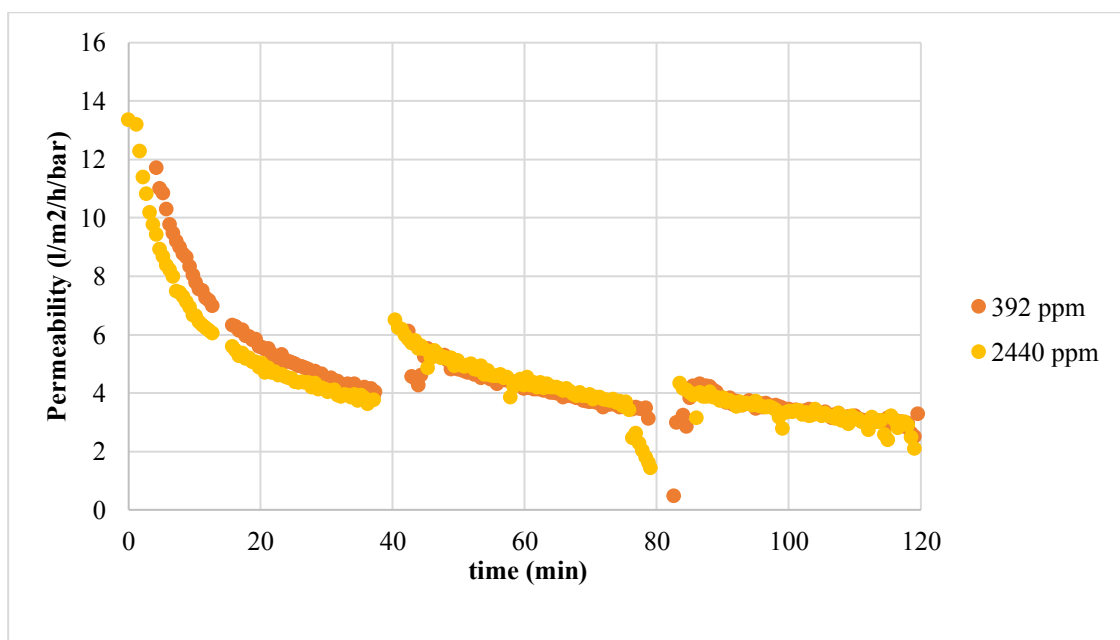


Figure C2. 2400 and 400 mg/l iron hydroxide coating results

Table C1. Measured iron coated concentration and calculated surface area

	Iron Dosage Concentration (mg/l)	
	2440	392
Iron (II/III) feed concentration (mg/l)	403	42
Iron (II/III) coated (mg)	701.82	109.2
Surface area of iron (m ²)	42.1092	6.552

Appendix D

Calcium carbonate coating experiment results

D1. Blank experiment result vs 400 mg/l calcium carbonate reaction

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Calcium concentration: 400 mg/l
- Coating duration: 10 minutes
- Coating pH: 10
- Citric acid concentration: 400 mg/l
- Cleaning duration: 15 minutes
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

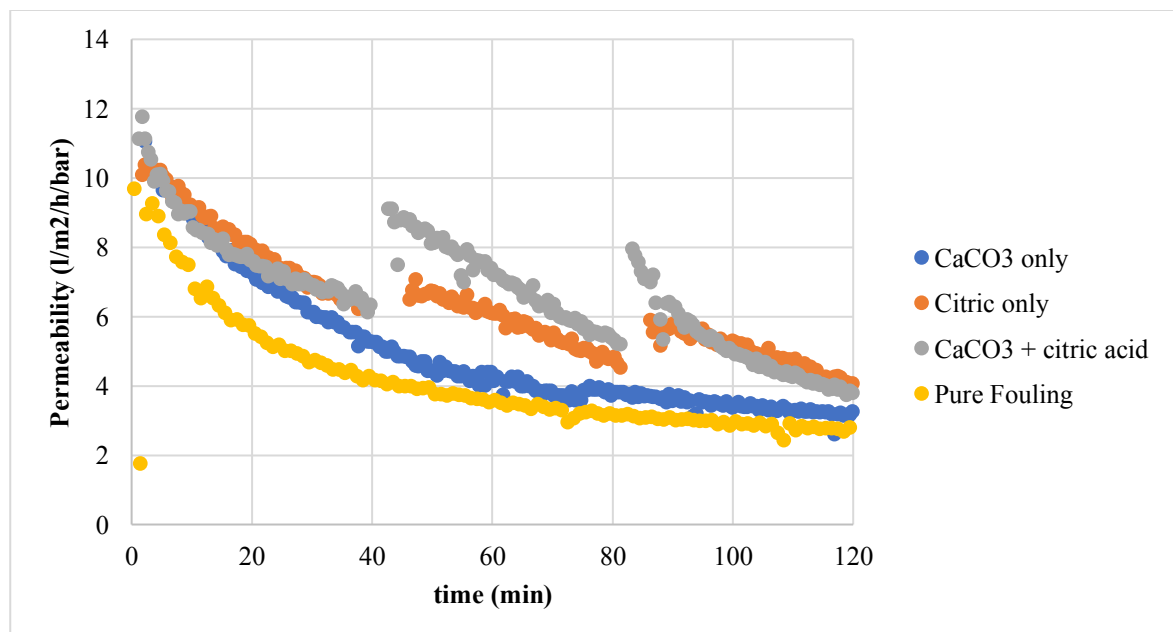


Figure D1. Permeability curve of blank experiment and 400 mg/l calcium carbonate reaction

D2. Cleaning with citric acid vs hydrochloric acid

Experimental condition:

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Calcium concentration: 400 mg/l
- Coating duration: 10 minutes
- Coating pH: 10
- Citric acid and hydrochloric acid concentration: 400 mg/l
- Cleaning duration: 15 minutes
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

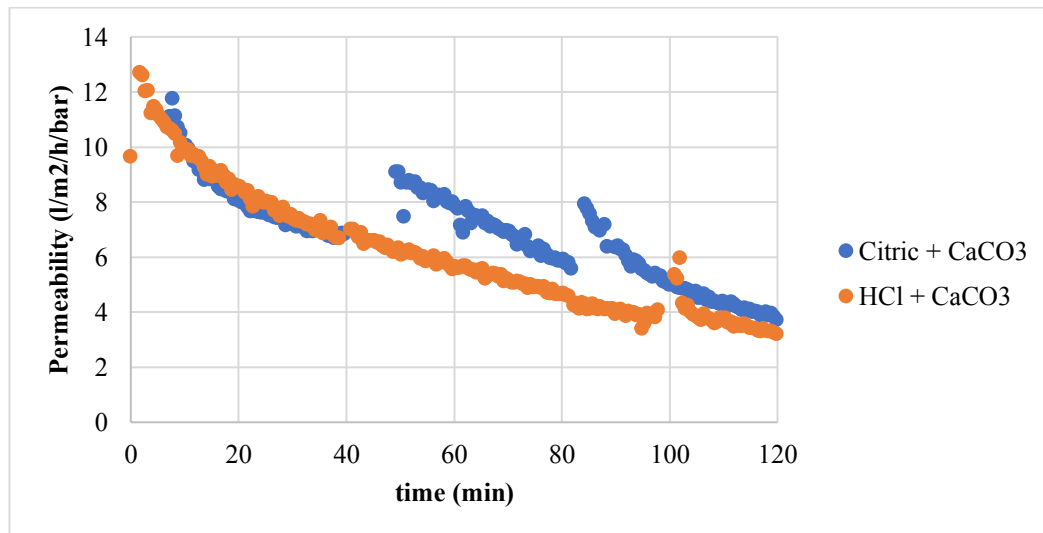


Figure D2. Permeability curve of hydrochloric acid and citric acid cleaning

D3. Dosing concentration investigation results

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Coating duration: 10 minutes
- Coating pH: 10
- Cleaning duration: 15 minutes
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

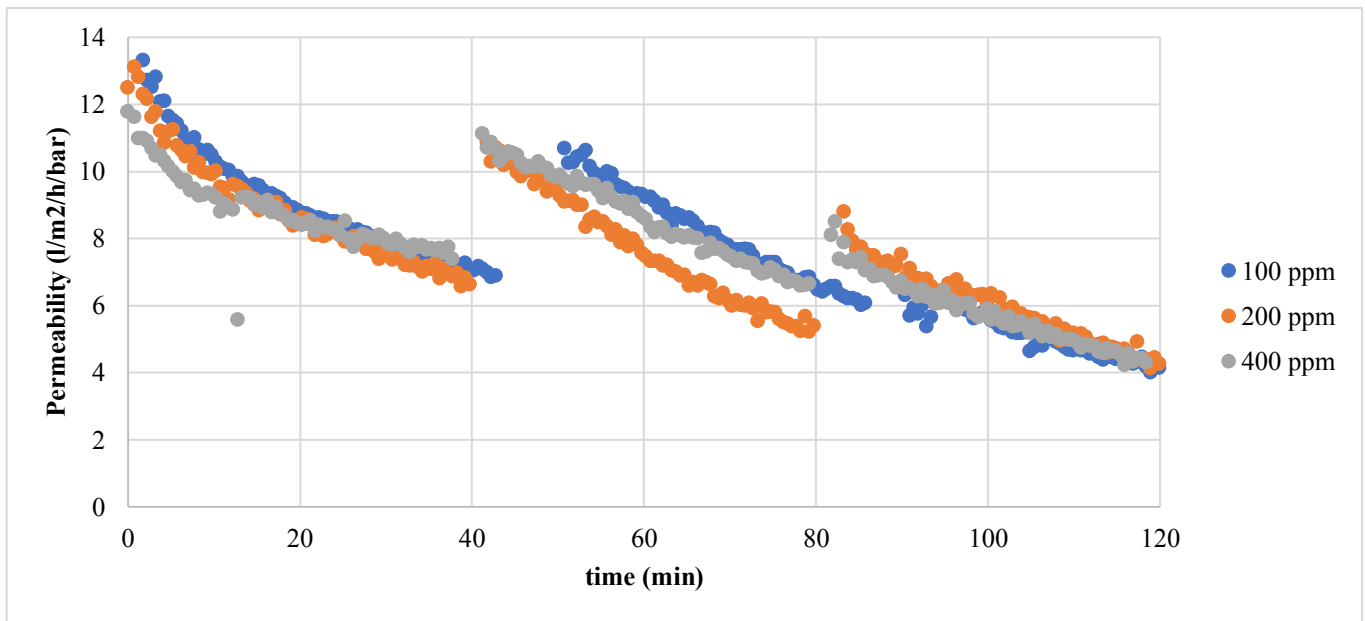


Figure D3. Permeability curve of different calcium carbonate dosing concentration

Table D1. Measure feed concentration and deposited calcium carbonate during dosing concentration experiment

	Feed concentration					
	400 mg/l		200 mg/l		100 mg/l	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Calcium feed concentration (mg/l)	44	53	37	33	12	14
Calcium coated (mg)	325.00	316.63	99.91	41.67	41.67	91.67

Table D2. Permeability recovery results of dosing concentration experiment

	Experiment	Recovery	
		1st Cleaning	2nd Cleaning
Cleaning Interval	100 mg/l	59	4
	200 mg/l	65	44
	400 mg/l	85	37

D4. Cleaning duration investigation results

- Filtration cross flow velocity: 1.1 m/s
- Pressure during alginate filtration: 5 bar
- Forward flush solution: Feed alginate solution
- Cleaning interval: 40 minutes
- Calcium concentration: 400 mg/l

- Coating duration: 10 minutes
- Coating pH: 10
- Citric acid concentration: 400 mg/l
- Forward flush cross flow velocity: 3 m/s
- Forward flush duration: 5 minutes

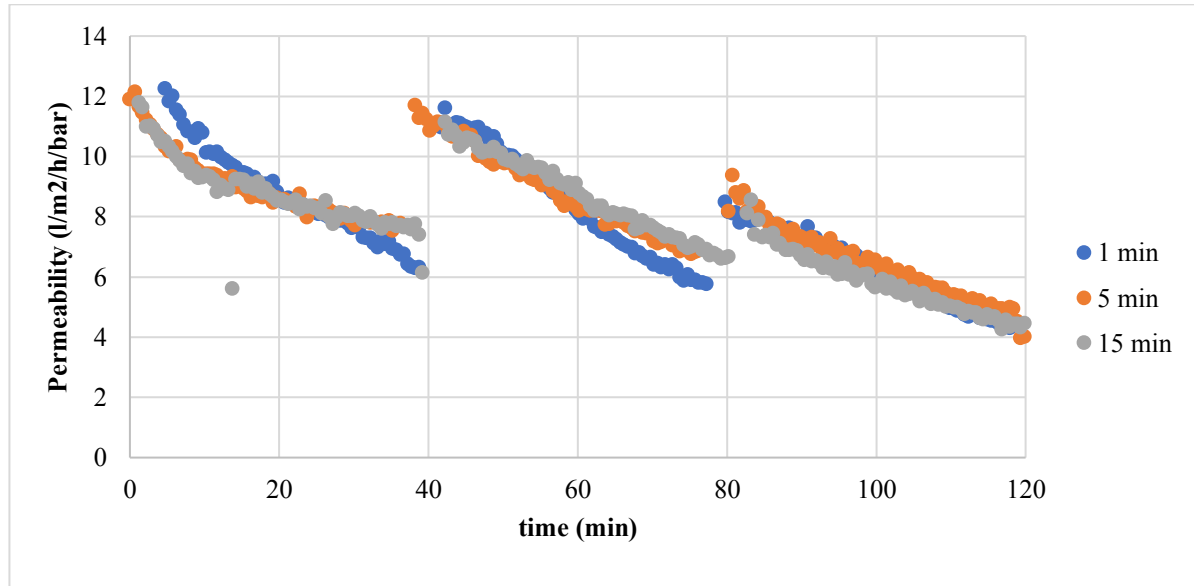


Figure D4. Permeability curve of different cleaning duration of calcium carbonate coating

Table D3. Measure feed concentration and deposited calcium carbonate during cleaning duration experiment

	Cleaning Duration (min)					
	1		5		15	
	First Coating	Second Coating	First Coating	Second Coating	First Coating	Second Coating
Feed concentration	59	46	108	124	44	53
Deposited calcium carbonate	391.67	241.67	316.67	350.00	325.00	316.63

Table D4. Permeability recovery results of cleaning duration experiment

	Experiment	Recovery	
		1st Cleaning	2nd Cleaning
Cleaning Duration	1 min	89	42
	5 min	95	48
	15 min	88	38

Appendix E

Iron hydroxide upscaling calculation

E1. Experimental data

Coating data

Table E1. Experimental coating process data

Parameter	unit	value	Source
Membrane surface area	m ²	0.001627	INOPOR data
iron dosage concentration	mg/l	400	Experimental setup
feed iron chloride concentration	mg/l	72	experimental result (1 st coating)
	mg/l	63	experimental result
volume of dosing solution	l	10	experimental result
Concentrate iron chloride concentration	mg/l	40	experimental result
coating duration	min	10	experimental setup
cross flow velocity during coating	m/s	0.36	experimental setup
volumetric flow rate	m ³ /s	0.00058572	experimental setup
Iron deposited on membrane surface			
first coating	mg	151.26	measured experimental result
second coating	mg	58.68	measured experimental result
total	mg	209.94	experimental result

Hydrogen peroxide data

Table E2. Required amount and concentration of citric acid during the experiment

Parameter	unit	value	Source
Hydrogen peroxide concentration	mg/l	400	experimental setup
required cleaning solution volume	l	1	experimental setup

Water production data

Table E3. Water production during the experiment

Parameter	unit	value	Source
feed water flow rate	kg/l	150	Experimental setup
Crossflow velocity	m/s	1.08	Experimental setup
concentrate flow rate	kg/l		
permeate weight	mg	23.36	Experimental results of 1 st coating
	mg	16.22	Experimental results of 2 nd coating

pressure	bar	5	Experimental setup
filtration duration	min	120	Experimental setup

Chemical cleaning with 0.1 % sodium hypochlorite data

Table E4. Required 0.1 % sodium hypochlorite during the experiment

Parameter	Units	Value	source
Sodium hypochlorite concentration	%	0.10	experimental setup
Stock solution concentration	mg/l	60	experimental setup
total solution volume	l	0.5	experimental setup
volume of stock solution	ml	8	experimental setup
cleaning duration	hour	1	experimental setup

Filtration duration data

Table E5. Duration of every process involves in the experiment

Parameter	Units	Value	source	notes
Alginate filtration	minutes	120	experimental setup	
iron chloride coating duration	minutes	20	experimental setup	two coating per experiment
Hydrogen peroxide cleaning duration	minutes	20	experimental setup	two cleaning per experiment
Forward flush cleaning duration	minutes	10	experimental setup	two coating per experiment
Sodium hypochlorite cleaning	hours	1	experimental setup	1 chemical cleaning per experiment

E2. Upscaling calculation data

Upscaling factor

Table E 6. Upscaling factor for projection of experimental data to real sewage water filtration

Parameter	Units	Value	Source	Notes
real crossflow velocity	m/s	1	Kramer et al. 2015	
Real membrane surface area	m ²	1	Kramer et al. 2015	
real volumetric flow rate	m ³ /s	1		cross flow velocity x area
linearization factor		614.63		Large membrane / small membrane

Upscaled coating data

Table E7. Data of coating parameter projected using linearization factor

Parameter	Units	Value	Source	Notes
Membrane surface area	m ²	1	Kramer et al. 2015	
iron chloride dosing concentration	mg/l	400	Experimental result	
feed iron chloride concentration	mg/l	72		
	mg/l	63	experimental result	
volume of dosing solution	l	6146.28		Experimental result * linearization
Concentrate iron chloride concentration	mg/l			
coating duration	min	10		similar duration as in experiment
flow rate during coating	l/h	221.27		cross flow velocity upscale = experiment
iron deposited on the membrane surface				
first coating	kg	0.09		experiment x linearization
second coating	kg	0.04		experiment x linearization
total	kg	0.13		

Upscaled cleaning data

Table E8. Required hydrogen peroxide to clean large membrane

Parameter	Units	Value	Source	Notes
Hydrogen peroxide concentration	mg/l	400		similar concentration as in experiment
Required cleaning solution volume	l	0.44		2 x void volume of membrane

Upscaled water production data

Table E 9. Water production of real sewage water filtration

Parameter	Units	Value	Source	Notes
Membrane flux	l/m ² h	30	Experimental results	Water productivity of small membrane/area of small membrane
system recovery	%	50	Kramer et al. 2015	
feed flow rate	l/h	40		Based on membrane flux and recovery
concentrate flow rate	l/h	20		Based on membrane flux and recovery

filtration duration	h	120	Kramer et al. 2015	
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Cleaning Interval in Upscaled experiment

Table E10. Duration of each process involved in 1 set of experiment

Parameter	Units	Value	Source	Notes
total filtration time in experiment	hours	2.83		1 set of experiment
total process time in plant	hours	120.00	Kramer et al. 2015	3 filtration, 2 cleaning with citric acid and 1 cleaning with NaOCl
total filtration duration in plant	hours	118.17		assumed cleaning duration similar with the experiment (total process duration – cleaning duration)
cleaning interval in plant	hours	39.39		duration of 1 cleaning interval before cleaning required (total filtration duration/3)

Sodium hypochlorite cleaning

Table E11. Required sodium hypochlorite to clean large membrane

Parameter	Units	Value	Source	Notes
Sodium hypochlorite concentration	%	0.00	experimental setup	
Stock solution concentration	mg/l	60	experimental setup	
total solution volume	l	0.44	experimental setup	2 x void volume of membrane
cleaning duration	hour	1.00		similar duration as in lab experiment

Upscaled process duration

Table E12. Upscaled process duration

Parameter	Units	Value	Source	Notes
Alginate filtration	hours	118.17		total filtration time as mentioned in paper subtract by cleaning time
iron chloride coating duration	hours	0.33		similar duration as in lab experiment
Hydrogen peroxide cleaning duration	hours	0.33		similar duration as in lab experiment
Forward flush cleaning duration	hours	0.17		similar duration as in lab experiment

Sodium hypochlorite cleaning	hours	1.00		similar duration as in lab experiment
total duration	hours	120.00	Kramer et al. 2015	
Effective filtration time	hours/year	8626.17		total time in which membrane produced water
required coating set peryear	/year	73.00		number of coating done in 1 year (2 coating per set)
Frequency of peroxide cleaning	/year	73.00		number of peroxide cleaning in 1 year (2 coating per set)
Effective forward flush cleaning time	hours/year	12.17		total duration of forward flush in 1 hour

Yearly water production and resource consumption

Table E13. Yearly water production and resource consumption

Parameter	Units	Value	Source	Notes
produced water	m3/year	268.13		membrane flux x effective filtration duration
required iron chloride for coating	kg/year	9.42		Amount of iron required in 1 set of filtration x number of filtration set in 1 year
required peroxide solution	m3/year	0.0320		400 mg/l concentration (required volume x number of operation cycle in 1 year x 2)
	kg/year	0.0128	pure peroxide	
required hypochlorite	m3/year	0.0320		(required volume x number of operation cycle in 1 year x 2)
	kg/year	0.3201		

Appendix F

Calcium carbonate upscaling calculation

F1. Experimental data

Coating data

Table F1. Experimental coating process data

Parameter	unit	value	Source
Membrane surface area	m ²	0.001627	INOPOR data
Calcium carbonate dosage concentration	mg/l	200	Experimental setup
feed calcium carbonate concentration	mg/l	49	experimental result
	mg/l	75	experimental result
volume of dosing solution	l	10	experimental result
Concentrate calcium carbonate concentration	mg/l	25	
coating duration	min	10	Experimental setup
cross flow velocity during coating	m/s	0.36	Experimental setup
volumetric flow rate	m ³ /s	0.00058572	Experimental setup

Calcium carbonate deposited on the membrane surface

Table F2. Measured amount of calcium carbonate deposited on the membrane surface

Parameter	unit	value	Source
first coating	mg	141.67	experimental result
second coating	mg	47.40	experimental result
total	mg	189.07	experimental result

Citric acid cleaning data

Table F3. Required amount and concentration of citric acid during the experiment

Parameter	unit	value	Source
citric acid concentration	mg/l	200	experimental setup
required cleaning solution volume	l	1	experimental setup

Water production data

Table F4. Water productivity during the experiment

Parameter	unit	value	Source
feed water flow rate	kg/l	150	Experimental setup
Crossflow velocity	m/s	1.08	Experimental setup
concentrate flow rate	kg/l		
permeate weight	mg	27.72	1st coating
	mg	20.26	2nd coating
pressure	bar	5	Experimental setup
filtration duration	min	120	Experimental setup

Chemical cleaning with 0.1 % concentration data

Table F5. Required amount and concentration of sodium hypochlorite during coating

Parameter	Units	Value	source
Sodium hypochlorite concentration	%	0.10	experimental setup
Stock solution concentration	mg/l	60	experimental setup
total solution volume	l	0.5	experimental setup
volume of stock solution	ml	8	experimental setup
cleaning duration	hour	1	experimental setup

Experiment duration data

Table F6. Duration of every process involves during the experiment

Parameter	Units	value	source	notes
Alginate filtration	minutes	120	experimental setup	
calcium carbonate coating duration	minutes	20	experimental setup	two coating per experiment
citric acid cleaning duration	minutes	2	experimental setup	two cleaning per experiment
Forward flush cleaning duration	minutes	10	experimental setup	two coating per experiment
Sodium hypochlorite cleaning	hours	1	experimental setup	1 chemical cleaning per experiment

F2. Upscaling calculation data

Upscaling Factor

Table F7. Upscaling factor to project experimental result on larger scale operation

Parameter	units	value	source	notes
real crossflow velocity	m/s	1	Kramer et al. 2015	
Real membrane surface area	m ²	1	Kramer et al. 2015	
real volumetric flow rate	m ³ /s	1		cross flow Velocity x area
linearization factor		614.63		Large membrane/small membrane

Upscaled coating data

Table F8. Data of coating parameter projected using linearization factor

Parameter	Units	value	source	notes
Membrane surface area	m ²	1	Kramer et al. 2015	
calcium carbonate dosing concentration	mg/l	200	Experimental result	
feed calcium carbonate concentration	mg/l	49	experimental result	
	mg/l	75	experimental result	
Concentrate calcium carbonate concentration	mg/l	20	experimental result	
coating duration	min	10		similar duration as in experiment
flow rate during coating	l/h	221.27		cross flow velocity upscale = experiment

Upscaled calculation of calcium carbonate deposited on the membrane surface

Table F9. Deposited calcium carbonate on large membrane

Parameter	Units	value	source	notes
calcium carbonate deposited on membrane surface				
first coating	kg	0.09		experiment x linearization
second coating	kg	0.03		experiment x linearization
total	kg	0.12		

Upscaled citric acid cleaning data

Table F10. Required citric acid to clean large membrane

Parameter	Units	value	source	notes
citric acid concentration	mg/l	200		similar concentration as in experiment
required cleaning solution volume	l	0.438501		2 x membrane void volume = 2 x number of channel x volume of each channel

Upscaled clean water productivity data

Table F11. Water production using large membrane

Parameter	Units	value	source	notes
Membrane flux	l/m ² h	40	Experimental result	Water productivity of small membrane/area of small membrane
system recovery	%	50	Kramer et al. 2015	
feed flow rate	l/h	40		Based on membrane flux and recovery
concentrate flow rate	l/h	20		Based on membrane flux and recovery
Total filtration duration	h	120	Kramer et al. 2015	3 filtration, 2 cleaning with citric acid and 1 cleaning with NaOCl

Sodium hypochlorite cleaning

Table F12. Required sodium hypochlorite to clean large membrane

Parameter	Units	value	source	notes
Sodium hypochlorite concentration	%	0.10	experimental setup	
Stock solution concentration	mg/l	60	experimental setup	
total solution volume	l	0.44		2 x membrane void volume = 2 x number of channel x volume of each channel
cleaning duration	hour	1.00		similar duration as in lab experiment

Upscaled alginate filtration duration data

Table F13. Duration of each process involves in filtration of real sewage water

Process duration	Units	value	source	notes
Alginate filtration	hours	118.47		total filtration time as mentioned in paper subtract by cleaning time
calcium carbonate coating duration	hours	0.33		similar duration as in lab experiment
citric acid cleaning duration	hours	0.03		similar duration as in lab experiment
Forward flush cleaning duration	hours	0.17		similar duration as in lab experiment
Sodium hypochlorite cleaning	hours	1.00		similar duration as in lab experiment
total duration	hours	120.00	Kramer et al. 2015	
Effective filtration time	hours/year	8648.1		total time in which membrane produced water
required coating set peryear	/year	73.00		number of coating done in 1 year (2 coating per set)
Frequency of citric acid cleaning	/year	73.00		number of citric acid cleaning in 1 year (2 coating per set)
Effective forward flush cleaning time	hours/year	12.17		total duration of forward flush in 1 hour

Yearly water production and resource consumption

Table F14. Yearly water production and resource consumption for real sewage water filtration

Parameter	Units	Value	Source	Notes
produced water	m ³ /year	352.12		membrane flux x effective filtration duration
required calcium carbonate for coating	kg/year	8.48		every 100 hours they required this much
required citric acid solution	m ³ /year	0.03	200 mg/l concentration	
	kg/year	0.01	pure citric acid	
required water for forward flush	m ³ /year	1794.71	Feed water for forward flush	
require hypochlorite soluion	m ³ /year	0.032	1 % citric acid volume	
	kg/year	0.320	pure citric acid	

Appendix G

0.1 % sodium hypochlorite upscaling calculation

G1. Experimental data

Water production data

Table G1. Water productivity during the experiment

Parameter	unit	value	Source
Membrane surface area	m ²	0.001627	INOPOR data
feed water flow rate	kg/l	150	Experimental setup
Crossflow velocity	m/s	1.08	Experimental setup
concentrate flow rate	kg/l		
Pressure	bar	5	Experimental setup
filtration duration	min	120	Experimental setup

Chemical cleaning with 0.1 % concentration data

Table G2. Required amount and concentration of sodium hypochlorite during coating

Parameter	Units	Value	source
Sodium hypochlorite concentration	%	0.10	experimental setup
Stock solution concentration	mg/l	60	experimental setup
total solution volume	l	0.5	experimental setup
volume of stock solution	ml	8	experimental setup
cleaning duration	hour	3	experimental setup

Experiment duration data

Table G3. Duration of every process involves during the experiment

Parameter	Units	value	source	notes
Alginate filtration	minutes	120	experimental setup	
iron chloride coating duration	minutes	0	experimental setup	two coating per experiment
Hydrogen peroxide cleaning duration	minutes	0	experimental setup	two cleaning per experiment
Forward flush cleaning duration	minutes	10	experimental setup	two coating per experiment
Sodium hypochlorite cleaning	hours	3	experimental setup	1 chemical cleaning per experiment

G2. Upscaling calculation data

Upscaling Factor

Table G4. Upscaling factor to project experimental result on larger scale operation

Parameter	units	value	source	notes
real crossflow velocity	m/s	1	Kramer et al. 2015	
Real membrane surface area	m ²	1	Kramer et al. 2015	
real volumetric flow rate	m ³ /s	1		cross flow Velocity x area
linearization factor		614.63		Large membrane/small membrane

Upscaled clean water productivity data

Table G5. Water production using large membrane

Parameter	Units	value	source	notes
Membrane flux	l/m ² h	22.12	Experimental result	Water productivity of small membrane/area of small membrane
system recovery	%	50	Kramer et al. 2015	
feed flow rate	l/h	40		Based on membrane flux and recovery
concentrate flow rate	l/h	20		Based on membrane flux and recovery
Total filtration duration	h	120	Kramer et al. 2015	3 filtration, 2 cleaning with citric acid and 1 cleaning with NaOCl

Sodium hypochlorite cleaning

Table G6. Required sodium hypochlorite to clean large membrane

Parameter	Units	value	source	notes
Sodium hypochlorite concentration	%	0.1	experimental setup	
Stock solution concentration	mg/l	60	experimental setup	
total solution volume	l	0.14		2 x membrane void volume = 2 x number of channel x volume of each channel
cleaning duration	hour	1.00		similar duration as in lab experiment

Upscaled alginate filtration duration data

Table G7. Duration of each process involves in the filtration of real sewage water

Process duration	Units	value	source	notes
Alginate filtration	hours	116.83		total filtration time as mentioned in paper subtract by cleaning time
Forward flush cleaning duration	hours	0.17		similar duration as in lab experiment
Sodium hypochlorite cleaning	hours	1.00		similar duration as in lab experiment
total duration	hours	120.00	Kramer et al. 2015	
Effective filtration time	hours/year	8528.83		total time in which membrane produced water
Effective forward flush cleaning time	hours/year	12.17		total duration of forward flush in 1 hour

Yearly water production and resource consumption

Table G8. Yearly water production and resource consumption for real sewage water filtration

Parameter	Units	Value	Source	Notes
produced water	m ³ /year	1793.83		membrane flux x effective filtration duration
concentrate disposed by filtration	m ³ /year	170.58		Concentrate only be produced during effective filtration time
require hypochlorite soluion	m ³ /year	0.0032	1 % hypochlorite	
	kg/year	0.032	pure hypochlorite	

Appendix H

Operational cost calculation

H1. Operational cost for iron hydroxide

Table H1. Operational cost for iron hydroxide coating

Operational cost	Required amount per year	Units	Price per unit	Units	Total price per component (euro)	Price source
Electricity	224.19	kWh	0.17	eur/kwh	37.22	https://1-stromvergleich.com/electricity-prices-europe/
Iron chloride	9.42	kg	1.00	\$/kg	8.01	http://www.globexmining.com/TechInfo/IndustrialMineralsPrices_September2011.pdf
Hydrogen peroxide	0.01	kg	0.77	\$/kg	0.01	http://www.h2o2.com/faqs/FaqDetail.aspx?fld=25
sodium hypochlorite	0.03	m3	0.46	\$/L (12.5 %)	12.51	http://www.stpetersmo.net/16-164SodiumHypochloriteSolution12-5-051616.pdf
Total operation price				euro	57.74	
				euro/m3	0.22	

H2. Operational cost for calcium carbonate

Table H2. Operational cost for calcium carbonate coating

Operational cost	Required amount per year	Units	Price per unit	Units	Total price per component (Euro)	Price source
Electricity	170.71	kWh	0.166	eur/kwh	28.34	https://1-stromvergleich.com/electricity-prices-europe/
Calcium carbonate solution	8.48	kg	0.35	\$/kg	2.52	http://www.globexmining.com/TechInfo/IndustrialMineralsPrices_September2011.pdf
Citric acid	0.01	kg	0.7	\$/kg	0.01	https://www.alibaba.com/product-detail/Raw-Material-Bulk-Citric-Acid_60747484453.html?spm=a2700.7724857.main07.19.4f3f1e3713AGuK&s=p
Sodium hypochlorite	0.03	m3	0.459709379	\$/L (12.5 %)	12.51	http://www.stpetersmo.net/16-164SodiumHypochloriteSolution12-5-051616.pdf
Total operation price				euro/year	43.38	
				euro/m3	0.12	

H3. Operational cost for 0.1 % sodium hypochlorite cleaning

Table H3. Operational cost for calcium carbonate coating

Operational cost	Required amount per year	Units	Price per unit	Units	Total price per component (Euro)	Price source
Electricity	320.46	kWh	0.166	euro/kwh	53.20	https://1-stromvergleich.com/electricity-prices-europe/
Sodium hypochlorite	0.03	m3	0.46	\$/L (12.5 %)	12.51	http://www.stpetersmo.net/16-164SodiumHypochloriteSolution12-5-051616.pdf
Total operation price				euro/year	65.71	
				euro/m3	0.33	

Appendix I

Input data for LCA calculation

I1. Iron hydroxide coating Input and output component data

Table I1. Mass balance data of membrane filtration process using iron hydroxide coating

Process 1	membrane filtration		
Products In	Value	units	Source
Sewage water(Alginate)	343.976	m3/year	Upscaling calculation result
Iron chloride	9.42	kg/year	Upscaling calculation result
Hydrogen peroxide	0.03201	m3/year	Upscaling calculation result
Sodium hypochlorite	0.032010573	m3/year	Upscaling calculation result
Products out			
Clean water	171.99	m3/year	Upscaling calculation result
Extension Out			
Iron chloride	9.42	kg/year	Upscaling calculation result
Hydrogen peroxide	0.03	m3/year	Upscaling calculation result
Sodium hypochlorite	0.032010573	m3/year	Upscaling calculation result
Extension In			Upscaling calculation result
Electricity	0.8	kWh/m3 feed	[92]

Table I2. Mass balance data of fuel production

Process 2	Fuel Production		
	Value	units	Source
Products out			
Fuel	1	L	[84]
Extension in			
Crude oil	2.22	L	[84]
Extension out			
Carbon dioxide	0.3	kg/L fuel	[84]
Sulphur dioxide	0.0083	kg/L fuel	[84]

Table I3. Mass balance data of electricity production

Process 3	Electricity production		
			[93]
Product out			[93]
Electricity	1	kwh	[93]
Products in			
Fuel	0.093	L	[93]
Extension out			
Carbon dioxide	0.674	kg/kwh	[93]
Sulphur dioxide	0.000616	kg/kwh	[93]

Table I4. Mass balance data of hydrogen peroxide disposal

Process 4	hydrogen peroxide addition		
Production out			
hydrogen peroxide	1	kg	
Extention out			
carbon dioxide	2.49	kg-CO2/kg Hydrogen peroxide	[94]
ecotoxicity	3.83	kg dcb	[95]

Table I5. Result of CMLCA categorization and normalization

Categorization	Value	Units
Carcinogenic effects on human	6.4×10^{-7}	DALY
Respiratory effect caused by inorganic substances	1.6×10^{-9}	DALY
Damages to human health caused by climate change	2.1×10^{-8}	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	1.2×10^{-2}	PDF*m2*yr
Damages to resources caused by mineral extraction	1.8×10^{-3}	MJ
Damages to resources caused by fossil fuel extraction	0.51	MJ
Normalization factor	Value	Units
Human Health	0.0154	DALY
Ecotoxicity	5130	PDF*m2*yr
Resources (MJ/yer)	8410	MJ
Weighting Factor	Value	Units
Human health	0.4	
Ecosystem quality	0.4	
resources	0.2	
total score	3.0212E-05	

I2. Calcium carbonate coating Input and output component data

Table I6. Mass balance data of membrane filtration process using calcium carbonate coating

Process 1	MEMBRANE FILTRATION		
Products In	Value	units	Source
Sewage water(Alginate)	345.92	m3/year	Upscaling calculation result
Calcium carbonate	8.48	kg/year	Upscaling calculation result
Citric acid	0.03	m3/year	Upscaling calculation result
Sodium hypochlorite	0.032	m3/year	Upscaling calculation result
Products out			
Clean water	172.96	m3/year	Upscaling calculation result
Extension Out			
Calcium carbonate	8.48	kg/year	Upscaling calculation result
Citric acid	0.01	kg/year	Upscaling calculation result
Sodium hypochlorite	0.03201	m3/year	Upscaling calculation result
Extension In			Upscaling calculation result
Electricity	0.8	kWh/m3 feed	[96]

Table I7. Mass balance data of fuel production

Process 2	FUEL PRODUCTION		
	Value	units	
Products out			[84]
Fuel	1	L	
Extension in			
Crude oil	2.22	L	85]
Extension out			
Carbon dioxide	0.3	kg/L fuel	[84]
Sulphur dioxide	0.0083	kg/L fuel	[84]

Table I8. Mass balance data of electricity production

Process 3	ELECTRICITY PRODUCTION		
	value	units	source
Product out			
Electricity	10	kwh	[93]
Products in			
Fuel	2	kg	[93]
Extension out			
Carbon dioxide	1	kg/kwh	[93]
Sulphur dioxide	0.1	kg/kwh	[93]

Table I9. Mass balance data of citric acid disposal

Process 4	CITRIC ACID DISPOSAL		
Production out			
hydrogen peroxide	1	kg	
Extension out			
carbon dioxide	0.41	kg-CO2/kg Hydrogen peroxide	[97]
ecotoxicity	Not toxic to acid environment		[98]

Table I10. Result of CMLCA categorization and normalization

Categorization	Value	Units
Carcinogenic effects on human	1.18.E-09	DALY
Respiratory effect caused by inorganic substances	3.71.E-07	DALY
Damages to human health caused by climate change	1.22.E-08	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	7.07.E-03	PDF*m2*yr
Damages to resources caused by fossil fuel extraction	2.93.E-01	MJ
Normalization factor		
Human Health	0.0154	DALY
Ecotoxicity	5130	PDF*m2*yr
Resources (MJ/yer)	8410	MJ

Weighting Factor		
Human health	0.4	
Ecosystem quality	0.4	
resources	0.2	
total score	1.7503E-05	

I3. 0.1 % sodium hypochlorite cleaning input and output component data

Table I11. Mass balance data of membrane filtration process using 0.1 % sodium hypochlorite cleaning

Process 1	MEMBRANE FILTRATION		
Products In	Value	units	Source
Sewage water(Alginate)	400.58	m3/year	Upscaling calculation result
Sodium hypochlorite	0.032	m3/year	Upscaling calculation result
Products out			
Clean water	200.29	m3/year	Upscaling calculation result
Extension Out			
Sodium hypochlorite	0.096	m3/year	Upscaling calculation result
Extension In			Upscaling calculation result
Electricity	0.8	kWh/m3 feed	[96]

Table I12. Mass balance data of fuel production

Process 2	FUEL PRODUCTION		
	Value	units	
Products out			[84]
Fuel	1	L	
Extension in			
Crude oil	2.22	L	85]
Extension out			
Carbon dioxide	0.3	kg/L fuel	[84]
Sulphur dioxide	0.0083	kg/L fuel	[84]

Table I13. Mass balance data of electricity production

Process 3	ELECTRICITY PRODUCTION		
	value	units	source
Product out			
Electricity	10	kwh	[93]
Products in			
Fuel	2	kg	[93]
Extension out			
Carbon dioxide	1	kg/kwh	[93]
Sulphur dioxide	0.1	kg/kwh	[93]

Table I14. Result of CMLCA categorization and normalization

Categorization	Value	Units
Carcinogenic Effect on Humans	2.1E-09	DALY
Respiratory effect caused by inorganic substances	0.00000122	DALY
Damages to human health caused by climate change	4.03E-08	DALY
Damages to ecosystem quality caused by combined effect of acidification and eutrophication	0.0223	PDF*m2*yr
Damages to resources caused by fossil fuel extraction	0.968	MJ
Normalization factor		
Human Health	0.0154	DALY
Ecotoxicity	5130	PDF*m2*yr
Resources (MJ/yer)	8410	MJ
Weighting Factor		
Human health	0.4	
Ecosystem quality	0.4	
resources	0.2	
total score	5.7631E-05	